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# The Conductivity of Liquids

Methods, Results, Chemical Applications and Theoretical Considerations

By

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# THE CONDUCTIVITY OF LIQUIDS.

## CHAPTER I.

### Units. Methods for Determining Conductivity.

**THE KOHLRAUSCH SYSTEM OF UNITS.**—Conductivity is always determined by measuring its reciprocal resistance. Conductivity is, therefore, always defined in terms of units of resistance. Until recently the Siemens mercury unit has been the basis of the unit of conductivity of solutions, and, in fact, of all liquid conductors. This, in turn, has been very generally reproduced from the conductivities of various standard solutions, which values, as given by different authorities, have not always been identical. Within a few years, however, Kohlrausch and associates[1] have proposed a standard unit of conductivity based on the ohm and have determined with great care the conductivities of many standard solutions in terms of this unit. It is, consequently, very easy to reproduce and has now been very generally adopted by both physicists and chemists.

This **unit of conductivity** is defined as the conductivity of a column of liquid 1 cm. in length and 1 sq. cm. in cross section, which has a resistance of 1 ohm. Conductivity expressed in terms of this unit is called the **specific conductivity** and is designated by $\kappa$. The conductivity of a solution, which depends almost entirely on the dissolved substance, is, however, best expressed by means of the equivalent conductivity, which takes into account the concentration.

The **equivalent concentration** $\eta$ is the fraction of a gram-equivalent of the solute in 1 cc. solution. The **dilution** $\varphi$ is the reciprocal of this, that is $\varphi = \frac{1}{\eta}$ and is the number of cubic centimeters in which a gram-equivalent of the solute is dissolved. Since in most cases $\eta$ and $\varphi$ are rather cumbersome numbers, it is customary in referring to the concentration of a solution to give

[1] Kohlrausch, Holborn, and Diesselhorst: *Wied. Ann.*, 64, 417 (1898).

in their stead $m$ and $v$, respectively. These quantities are based on 1 liter of solution, so that $m = 1000\eta$, and $v = \frac{\varphi}{1000}$. $m$ and $v$ sometimes refer to gram-molecules per liter instead of gram-equivalents. When they are used thus in this book, it will be so stated.

The **equivalent conductivity** $\Lambda$ equals the specific conductivity divided by the equivalent concentration or multiplied by the dilution, that is,

$$\Lambda = \frac{\kappa}{\eta}, \text{ or } = \varphi\kappa.$$

The **molecular conductivity** $M$ is sometimes given. This is equal to the specific conductivity divided by the molecular concentration. For monobasic substances the equivalent conductivity and the molecular conductivity are, of course, equal.

**UNITS FORMERLY EMPLOYED.**—Until recently the specific conductivity $k$ was the conductivity of a column of liquid 1 m. long and 1 sq. mm. cross section, referred to the conductivity of a column of mercury of the same dimensions (Siemens unit) as unit. The ohm equals 1.0630 Siemens unit. This unit of conductivity is, therefore, $100 \times 100 \times 1.0630$ times the new one, so that $\kappa = 10630k$. Occasionally specific conductivities are met with expressed in units in which the conductivity of a column of liquid 1 cm. long and 1 sq. cm. cross-section is referred to the Siemens unit. Conductivity, expressed in this way, will be designated by $l$,[1] consequently

$$\kappa = 1.0630l.$$

The equivalent conductivity, when based on the Siemens unit, has been commonly designated by $\lambda$ and the molecular conductivity by $\mu$. Since concentrations were formerly almost invariably expressed in liters instead of cubic centimeters, it was convenient to multiply the small numbers obtained by $10^7$, so that

$$\lambda = 10^7 \frac{k}{m};$$

and, therefore,

[1] The symbols which have been used by different authorities to indicate conductivities referred to the Siemens unit have been very much at variance. See preface.

$$\Lambda = 1.0630\lambda, \text{ and } M = 1.0630\mu.$$

In Kohlrausch's earlier work $\lambda = 10^3 \frac{k}{m}$, and consequently here

$$\Lambda = 0.1063\lambda.$$

Although 1.0630 is theoretically the factor for converting conductivities expressed in units based on the Siemens unit into those expressed in the new units, the factor actually required is, in most cases, a little greater than this. It is 1.0690 for most of the work which has originated with Kohlrausch and his associates. The last equation in the preceding paragraph should, therefore, really be

$$\Lambda = 0.1069\lambda, \text{ or } = 0.1069\frac{k}{m}.$$

The factor is 1.066 for most of the work from Ostwald's laboratory. More exact information concerning this factor can be found in the paper by Kohlrausch, Holborn and Diesselhorst, referred to above. The conductivities of the more important solutions have been recalculated by Kohlrausch and Holborn and are given, expressed in the new units, in their *Leitvermögen der Elektrolyte*. Most of the recent conductivity results will be found in the appendix to this book.

**ABSOLUTE UNITS.**—Absolute electromagnetic units (C. G. S.) are sometimes employed, especially in formulating certain theoretical relations. In this system the unit of current strength = 10 amperes, the unit of potential = $10^{-8}$ volts and the unit of resistance = $10^{-9}$ ohms. If $K$ represents the electrical conductivity of a liquid when the unit is the conductivity of a cubic centimeter whose resistance is $10^{-9}$ ohms, then

$$K = 10^{-9}\kappa.$$

**RESISTANCE CAPACITY.**—Since the vessel in which the conductivity of a liquid is measured is never of standard dimensions, it is always necessary to introduce a factor to reduce the resistance actually measured to conductivity expressed in the proper units. The factor is called the **resistance capacity,** or sometimes simply the **capacity,** of the vessel and is designated by $C$. The

resistance $R$ of a column of liquid 1 cm. in length and 1 sq. cm. in cross section is, according to definition, equal to $\frac{1}{\kappa}$ ohm. If the column is $l$ cm. long and $s$ sq. cm. cross-section and the electrodes entirely fill the cross-section, obviously

$$R = \frac{1}{\kappa}\frac{l}{s} \text{ ohm},$$

or

$$\kappa = \frac{l}{s}\frac{1}{R}.$$

The resistance capacity $C$ is, therefore, equal to $\frac{l}{s}$, that is,

$$\frac{l \text{ cm.}}{s \text{ cm.}^2} = C \text{ cm.}^{-1}$$

Consequently the dimensions of the resistance capacity are reciprocal centimeters. In general for any vessel

$$\kappa = \frac{C}{R}.$$

Since $C$ is expressed in reciprocal centimeters, and $R$ in ohms, the dimensions of the specific conductivity are $\frac{1}{\text{cm.} \times \text{ohm}}$.

**TEMPERATURE.**—The conductivity of most solutions changes about 2 per cent. for each degree of temperature, and the temperature coefficient of many pure liquids is even greater than this. It is, therefore, essential when determining conductivity that the temperature remain constant and that it be expressed in terms of some fixed standard. The hydrogen scale is the standard commonly employed, and all temperatures given in this book are based on that scale. At 18° an accurate mercury thermometer of Jena normal glass registers about 0.1° too high (see Chapter IX).

## METHODS FOR DETERMINING CONDUCTIVITY.

**CLASSIFICATION.**—Methods for determining the conductivity of solutions are simply methods for measuring resistance applied to liquid media. They are of three classes: (1) Methods in which a direct current traverses the solution; (2) methods in which an

alternating current traverses the solution; (3) indirect method in which no electrodes are used, the solution being simply exposed to the influence of a strong electromagnetic field[1]. This last method has only become of theoretical interest, so it will not be further considered.

When a direct current is passed through a solution, polarization takes place upon the electrodes, and unless this can be eliminated it seriously interferes with the accurate determination of the conductivity. Various means have been employed to try to compensate this polarization, but very few of the methods so devised for determining conductivity compare in accuracy and rapidity with those in which alternating currents are employed. Recently, however, a method of this class has been described by Stroud and Henderson,[2] for which certain advantages are claimed over methods of the second class.

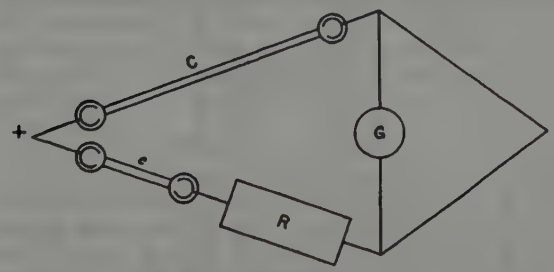



Fig. 1.

**STROUD AND HENDERSON'S METHOD.**—The method depends on the elimination of polarization on the electrodes by the employment of two electrolytic cells of similar form, but of different resistance capacity in two adjacent branches of a Wheatstone bridge and balancing the difference of resistance between them by means of suitable known resistances. This principle was not new at this time, but the value of Stroud and Henderson's application of it lies in the simplicity of their apparatus and in the accuracy with which measurements can be made.

[1] Guthrie and Boys: *Phil. Mag.* (5), 10, 326 (1880).

[2] *Phil. Mag.* (5), 49, 70 (1897).

The apparatus is arranged as in Fig. 1. $C$ and $c$ are two electrolytic cells of different capacity; $r$ and $r'$ are equal resistances of 1000 ohms each; $R$ is a rheostat containing resistances up to 20,000 or 30,000 ohms; $G$ is a D'Arsonval galvanometer.

Resistance is introduced at $R$ until the resistance of $c + R$ is, as nearly as possible, equal to that of $C$. Then, since $r$ and $r'$ are equal, equal currents are traversing $C$ and $c$, and, therefore, the polarization in each cell should be equal. These polarizations are opposed and in theory eliminated. It was found, as a matter of fact, that more than 99 per cent. of the polarization could be eliminated in this way. The rest could be drowned or at least reduced to insignificance by using high resistances and high voltages. With cells having a difference of resistance of about 20,000 ohms and with a resistance in the galvanometer of 300 ohms, good results were obtained with an electromotive force of 30 volts.

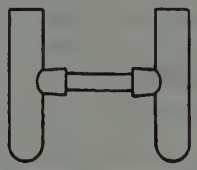


Fig. 2.

Cells giving the best results are of the form shown in Fig. 2. They consist of three parts, of which the two upright portions are small thick-walled test tubes with necks on the side. Into these necks fit the well-ground ends of a tube of, as nearly as possible, uniform bore. The diameter of the upright portions in Stroud and Henderson's apparatus was 1.2 cm. and the height 6 cm. The external diameter of the horizontal tube was 0.6 cm. The internal diameter was suited to the resistance of the electrolyte. In cell $C$ this tube was about 30 cm. long, and in $c$, 5 cm.

The relative resistance capacity of the two cells can be determined from the following data:

| | |
|---|---|
| Length of horizontal tube in $C$ | 29.70 cm. |
| Weight of mercury to fill same, plus watch glass | 29.836 grams. |
| Length of tube in $c$ | 4.89 cm. |
| Weight of mercury plus watch glass | 11.481 grams. |
| Density of mercury at temperature of experiment | 13.558 |

The difference between the resistance in $C$ and in $c$ is the resistance of the electrolyte in a tube, whose length is $29.70 - 4.89 = 24.81$ cm. The volume of this length of tube $= \frac{18.355}{13.558} = 1.354$ cc.

The resistance capacity $C$ therefore (page 4) equals $\frac{l}{s} = \frac{24.81 \times 24.81}{1.354} = 454.6$. This is the constant by which the reciprocal of the resistance is to be multiplied to give the specific conductivity of the electrolyte in reciprocal ohms.

The electrodes are of platinum foil in cylindrical form to fit the vertical tubes. To these are welded platinum wires, which are connected with the wires from the bridge by means of mercury cups.

One set of measurements, as made by Stroud and Henderson, with fifth-normal KCl is given below. The temperature of the cells was controlled by means of an oil-bath. The readings were all reduced to 18° by using the temperature coefficient 0.021 (see Chapter IX). The current was passed alternately in each direction.

| Direction of current. | Temperature. | Resistance. | Resistance reduced to 18°. |
|---|---|---|---|
| + | 18.26° | 21,035 | 21,149 |
| − | 18.19 | 21,045 | 21,129 |
| + | 18.17 | 21,015 | 21,119 |
| − | 18.11 | 21,065 | 21,113 |
| + | 18.08 | 21,085 | 21,120 |
| − | 18.06 | 21,095 | 21,121 |
| | | Mean, | 21,125 |

The specific conductivity of the solution therefore $= \kappa = \frac{C}{R} = \frac{454.6}{21,125} = 0.02152$. Since for a fifth-normal solution $\eta = 0.0002$, $\Lambda = 107.60$. Another solution of fifth-normal KCl, prepared independently from the above, gave $\Lambda = 107.18$. The agreement is good, and the authors conclude, from many considerations, that the errors in the method itself are small, much less than in the careful preparation of two solutions of the same concentration.

**OTHER METHODS OF THE FIRST CLASS.**—When the resist-

ance of the liquid is very great, around 100,000 ohms, its conductivity can be measured in a single cell by employing correspondingly great electromotive forces, as 100 volts. In such cases polarization can be neglected and measurements made similarly to above. $c$ is, of course, dropped out, and the ratio of $r$ to $r'$ is more conveniently made that of 1 to 10 or of 1 to 100. Cells of a form used by Stroud and Henderson are suitable. The electrodes should have a large surface and be covered with platinum black. The conductivity of good electrolytes can be measured in this way by using capillary tubes in the cell to increase the resistance. When making the readings the current should be on only for an instant.[1]

Fuchs (1875) originated a method with direct currents, whereby polarization on the electrodes can be avoided by making use of electrostatic measurement. A constant current is sent through a column of the electrolyte and through a known resistance. The potential difference is determined alternately with an electrometer at two cross-sections of the solution by means of secondary electrodes and at the ends of the known resistance. The circuit through the secondary electrodes acquires, under these conditions, only the slight current necessary to charge the electrometer. If in the former case the potential difference is found to be $V$ and in the latter case $V'$, letting $I$ be the current strength, we have the following relations:

$$V = IR \text{ and } V' = IR',$$

from which we obtain

$$R = \frac{R'V}{V'}.$$

The method is rather cumbersome, but yields good results.[2]

**METHOD OF KOHLRAUSCH.**—This belongs to the methods of the second class in which an alternating current traverses the electrolyte. Measurements are made by means of a Wheatstone bridge and the disappearance of the current in the cross branch is detected with a telephone. On account of the simplicity of the

[1] For further details concerning this method see the following: Kohlrausch and Heydweiller: *Wied. Ann.*, 53, 218 (1894); *Ibid.*, 54, 385 (1895); Warburg: *Ibid.*, 54, 396; Wildermann: *Ztschr. phys. Chem.*, 14, 247 (1894); Kohlrausch: *Ibid.*, 18, 126 (1894); Malmström: *Ibid.*, 22, 331 (1897).

[2] See in this connection Bouty and Foussereau: *J. de Phys.* (2), 4, 419 (1885); also Sheldon: *Wied. Ann.*, 34, 122 (1888).

apparatus required and the accuracy of the results obtained, this method is used more extensively than any other.

As commonly employed, the apparatus is arranged essentially as in Fig. 3. A current from the battery $B$ operates the induction apparatus $I$, whence an alternating current passes to the ends

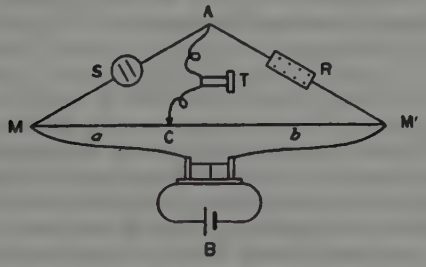



Fig 3.

of the bridge $M\,M'$. The resistance to be measured is placed in the branch $A\,M$, the known resistance $R$ in $A\,M'$. $M\,M'$ is a wire of as nearly uniform resistance as possible, along which slides the contact $C$. The telephone $T$ is in the cross-branch $A\,C$. A measurement is made by moving $C$ along $M\,M'$ until the telephone is either silent or gives a minimum tone, then the resistances are in the following proportion:

$$S:R = MC:CM'.$$

To insure the greatest accuracy $R$ should be made approximately equal to $S$, so that $C$ will be near the middle of $M\,M'$. From this proportion we have $S = R\,\frac{MC}{CM'}$, denoting the length $MC$ by $a$ and $CM'$ by $b$, then $S = R\,\frac{a}{b}$. If the wire $MM'$ is 1 meter (1000 mm.) in length, as is frequently the case, this equation becomes $S = R\,\frac{a}{1000-a}$, and much of the labor of computation can be saved by making use of Obach's tables (see appendix), which give for any value of $a$ the corresponding value of $\frac{a}{1000-}$.

Since the resistance of an electrolyte is given by the equation $S = R\frac{a}{b}$, the specific conductivity is given by

$$\kappa = \frac{C}{R\frac{a}{b}},$$

and for a wire 1 meter long this becomes

$$\kappa = \frac{C}{R\frac{a}{1000-a}},$$

in both of which $C$ is the resistance capacity of the electrolytic vessel. In order to illustrate the method of calculation, the results obtained with a tenth-normal solution of potassium chloride are given in the accompanying table. To insure greater accuracy, more than one reading (three in the table) are usually made at each concentration. Since the bridge wire is seldom of

CONDUCTIVITY OF TENTH-NORMAL KCl AT 18°.

$C = 0.1289$.

| $R$. Ohms. | $a$. mm. | $a$ corrected mm. | $\frac{a}{1000-a}$. | $\kappa$. |
|---|---|---|---|---|
| 8 | 592.0 | 590.2 | 1.4402 | 0.011188 |
| 10 | 535.8 | 535.0 | 1.1505 | 0.011204 |
| 12 | 489.6 | 489.8 | 0.9600 | 0.011189 |
| | | | Mean, | 0.011194 |

$$\Lambda = \frac{\kappa}{\eta} = 111.94$$

uniform resistance, as in this case, it is necessary to correct the readings $a$, as is seen in column 3, (see Chapter III). It is to be observed that the resistance $R$ was chosen so as to bring the readings near the middle of the bridge, that is, near 500. Under favorable conditions the quantity $a$ can be read accurately with a telephone to within from 0.1 to 0.3 mm. The method is seen, therefore, to be simple and quite accurate. Its rapidity is limited only by the time necessary for the solution in the electrolytic vessel to assume the temperature of the bath.

Variations of the method and different forms of apparatus which are sometimes employed, will be discussed in the next chapter.

**OTHER METHODS.**—Another method, which combines some features both of the first and of the second class, has been described by McIlhiney.[1] It consists in determining with a galvanometer the potential difference between the ends of a known resistance placed in series with the solution of unknown resistance. The current is supplied by a gravity battery, and before passing through the electrolyte it is transformed into an alternating current by means of a rotary pole changer, but the current passing through the known resistance and the galvanometer is direct. The method is fairly rapid, but is capable of only an approximate degree of accuracy.

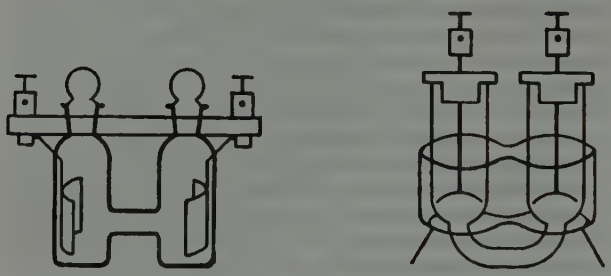
A method in many respects similar to McIlhiney's has been used recently by Morgan and Hildburgh.[2] In this an alternating current traverses the electrolyte, but is transformed into a direct current by means of a hydrogen rectifying cell before passing through the galvanometer. A small alternator was used by these investigators as the source of the current with excellent results.

1 *J. Am. Chem. Soc.*, 20, 206 (1898).
2 *J. Am. Chem. Soc.*, 22, 304 (1900).

## CHAPTER II.

### Apparatus Used in Determining Conductivity.

**ELECTROLYTIC VESSELS.**—These should be selected according to the resistance of the liquid under investigation. If the liquid is a good electrolyte, as fairly concentrated solutions of strong acids or bases or of most salts, vessels of the Kohlrausch type,



*a* *b*

Fig. 4.

as shown in Fig. 4, are the most suitable. Whatever the form of vessel employed, care should be exercised to keep the electrodes in as nearly the same position as possible, otherwise the resistance capacity may vary. In form *a* shown above, the electrodes are fused through the sides, so that their position is fixed. They should pass through the glass high enough so that they will not come in contact with the liquid of the temperature bath. The wires which come through should be fastened to binding posts on the support to prevent their being broken off. The covers of most electrolytic vessels are of ebonite, which is an excellent material for this purpose because it is a good insulator. In vessel Fig. 4*b*, the electrodes are usually adjusted so as just to rest in the narrow portion of the tubes, which tends to keep them in an invariable position. A small hole near the upper part of the concavity allows the escape of air or of electrolytic gas. The dimensions of a vessel should be suited to the resistance capacity desired. For capacities of from 1 to 5 cm.$^{-1}$, suitable dimensions for

form *b* are: diameter of vertical tubes, 15 mm.; diameter of connecting tube, 9 mm.; capacity up to the water mark, 15 to 30 cc. In form *a* the resistance capacity varies somewhat for different fillings of liquid. The height at which the liquid stands when the capacity is determined should, therefore, be marked on the glass, and whenever the vessel is used it should be filled to the same height.

For determining the conductivity of the so-called weak electrolytes, that is, solutions of comparatively low conductivity, as solutions of most organic acids or bases or dilute solutions of

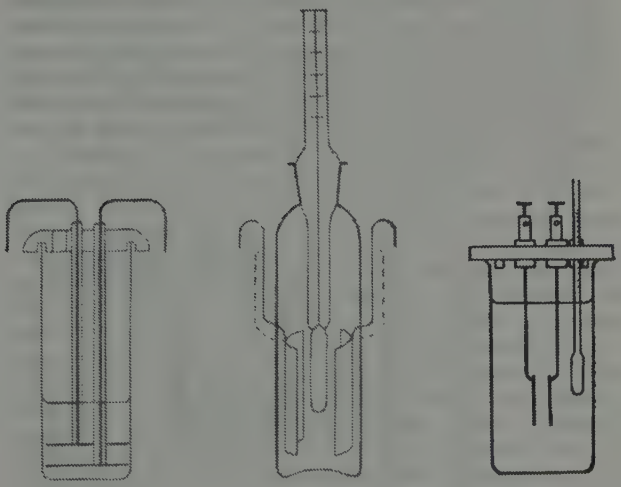


Fig. 5.

salts, vessels of the type shown in Fig. 5 should be used. Form *a*, due to Arrhenius, is one of the best, as it permits the electrodes to be set at any distance apart and the capacity thus changed at will. Care must, however, be exercised to keep them from slipping in the cover during use. A suitable size is about 8 cm. in height by 3 cm. in diameter. The electrodes fill the cross-section of the

vessel and the platinum wires connected with them are inclosed in glass capillary tubes. Connection is made with copper wires by means of mercury in the capillary tubes, or better, by soldering directly to the platinum wires of the electrodes. Forms *b* and *c* are due to Kohlrausch. The first is a small bottle from 10 to 100 cc. capacity, with semi-circular electrodes fused through the sides. It may be closed with a ground glass stopper, or better, with a small thermometer ground to fit the opening. Vessel *c* permits three different positions of the electrodes, so that the same vessel can be used for solutions of very different conductivities. The electrodes are nearest together in the position indicated in the figure, by turning one of them through 180° they are in the second position and somewhat farther apart, then by turning the other electrode through 180° a third position can be obtained in which the distance apart of the electrodes is the greatest.[1] For either one of these last two forms the resistance capacity must be determined for a definite filling, as with forms *a* and *b*, Fig. 4.

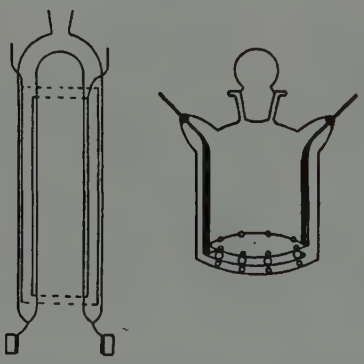


Fig. 6.

For very bad conductors, as distilled water and most organic liquids, it is advantageous to use other forms of vessels with still lower resistance capacities. Two such forms are shown in Fig.

[1] Loomis has devised a modification of this form of vessel, which permits accurate adjustment of the electrodes at any angle. See *Phys. Rev.*, 8, 258 (1899).

6, *a* and *b*. The first, due essentially to Pfeiffer, is made by fusing together two tubes so that they form a cylindrical vessel. The electrodes consist of concentric cylinders of platinum foil, one being against the inner glass wall and the other against the outer. The conducting wires are fused through the glass walls of the vessel. Form *b*, due to Schall, is somewhat similar to the Arrhenius vessel. The electrodes, however, are very close together and are held firmly apart by fusing short pieces of glass rod between them. The vessel can be closed with a ground glass stopper, or with a thermometer as in Fig. 5, *b*.

All glass used for making electrolytic vessels should be of good quality, very resistant to the action of water or to that of any other substance with which they may come in contact. Furthermore, such vessels should be steamed out or soaked out with warm water for a long period prior to use, especially if they are to be used for solutions whose conductivity is slight.

Vessels of variable resistance capacity of the form shown in Fig. 14, Chapter IV, are sometimes very advantageously employed. They are best adapted to the determination of the conductivity of concentrated solutions, where comparatively large resistance capacities are desired.

**ELECTRODES.**—Platinum is by far the most serviceable metal for electrodes. For measuring conductivity the electrodes are usually covered with platinum black, which tends to decrease polarization and to produce a sharper tone-minimum in the telephone when this instrument is employed. To insure a suitable kind of spongy coating on the electrodes the platinizing solution, suggested by Lummer and Kurlbaum, is commonly employed. This is a 3 per cent. solution of commercial platinum chloride ($H_2PtCl_6$) to which is added 0.025 per cent. of lead acetate. The process is best carried out directly in the electrolytic vessel, which is filled well over the electrodes[1] with this solution. The platinum deposits on the cathode. A suitable current can be obtained from two accumulators by introducing resistance from a rheostat until the evolution of gas is only moderate. In order to prevent excessive absorption of chlorine by the anode it is advisable to change

[1] The electrodes must be thoroughly cleaned beforehand with a strong solution of sodium hydroxide, then rinsed with distilled water several times, and not touched again with the hands before platinizing.

the direction of the current every few minutes. In this way a suitable deposit is formed on both electrodes in from ten to twenty minutes. Under any circumstances, however, some chlorine is held tenaciously by the electrodes. This can be removed by electrolyzing a dilute solution of sulphuric acid or of sodium acetate, the direction of the current being frequently changed. Finally, the electrodes should be washed off repeatedly with distilled water and left standing in water until used.

Fig. 7.

In certain cases blank electrodes are to be preferred. For example, they are better with concentrated solutions of strong acids and bases on account of the absorbent power of the platinum black of covered electrodes; with liquids which possess extraordinarily great resistance, as water of a high degree of purity; and with organic liquids, when it is found they are being oxidized on account of the presence of the platinum black. Blank elec-

trodes should always be thoroughly cleaned and finally rinsed with alcohol and dried before using.

Dip electrodes are sometimes very useful, especially when it is desired to measure the conductivity of a liquid in the bottle or other vessel in which it is preserved. According to Kohlrausch. the most useful form, Fig. 7, consists of two small platinum electrodes welded to platinum wires and these in turn inclosed in a capillary tube. Since such electrodes must have the same resistance capacity, regardless of the form of vessel in which they are used, they must be protected by a small glass bell fastened to the capillary in order to intercept the lines of force. A small hole near the top of the bell allows the escape of air or any gases formed.

**RESISTANCES.**—Every laboratory should possess a good resistance box having a sufficient variety of separate resistances. The wire of which the resistances are made should be non-inductively wound and have only a very small temperature coefficient. All resistances of standard make are now so constructed. The range of resistances in a box should be suited to the purpose for which it is to be employed. Resistances from 0.1 to 100 ohms are well adapted to use with concentrated solutions; for solutions of higher resistance they may range from 1 to 10,000 or even 50,000 ohms, while for general use in an electrochemical laboratory a box containing resistances from 1 to 10,000 ohms is very satisfactory. As to the number of separate resistances, 1, 10, 100, etc., ohms will answer. It is very convenient, however, to have a set so arranged that any resistance from 1 to 10,000 ohms can be obtained. Kohlrausch recommends sets of 1, 2, 7, 20, 70, 200, 700, 2000 and 7000 ohms as ample for most purposes.

A set of resistances should be calibrated before use by comparing the separate resistances with one another, and finally by comparing one of them with a standard resistance.

Graphite lines on ground glass are sometimes used as resistances. Such resistances are not designed to replace a resistance box. For high resistances, however, they are often more satisfactory, since they are free from capacity, which sometimes causes trouble with wire resistances. Every time such a graphite resistance is used it should be compared with some known resistance.

A preliminary calibration is not worth while on account of the irregular changes which graphite resistances seem to undergo.[1] Wildermann,[2] who gives excellent directions for the preparation of such resistances, found them to be sufficiently constant for his purpose.

**MEASURING BRIDGES FOR USE WITH ALTERNATING CURRENTS.**—The form most commonly employed, consisting of a wire 1 meter long, has already been described in connection with the Kohlrausch method for determining conductivity (Chapter I).[3] When great accuracy is not required, for laboratory instruction for example, a smaller combination bridge, represented in outline

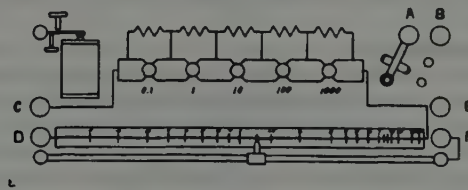



Fig. 8.

in Fig. 8, is very serviceable. The wire is only 25 cm. long, but is graduated so as to give directly the reading $\frac{a}{b}$. An induction coil and a resistance box are usually mounted on the same base, as is seen in the cut. The primary current is connected with the binding posts, *A*, *B*, the resistance to be measured with *C*, *D*, and the telephone with E, F.

Frequently greater accuracy is desired than can be obtained with a meter wire. In this case various means may be employed

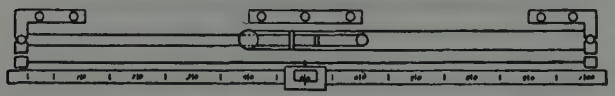


Fig. 9.

to lengthen the wire. The apparatus represented in Fig. 9 has,

[1] See Völlmer: *Wied. Ann.*, 32, 334 (1894).

[2] *Ztschr. phys. Chem.*, 14, 235 (1894).

[3] Such a bridge wire can be easily constructed. For directions see Ostwald and Luther: *Physico-chemische Messungen*, p. 346.

besides the primary meter wire, two secondary wires, each of which has the same resistance as the primary. One of the secondary wires can be connected with the left end of the primary wire, and the other with the right end. The wire can then be considered to be 3 meters long, and the ratio $\frac{a}{b}$ is obtained from the reading $a'$ on the primary wire, according to the following relation:

$$\frac{a}{b} = \frac{1000 + a'}{2000 - a'}.$$

If desired, a wire 2 meters long can also be obtained with this apparatus.

A second arrangement, whereby a wire of considerable length

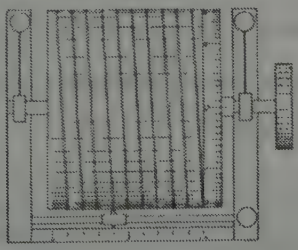


Fig. 10.

can be used, is represented in Fig. 10. In this case the wire is wound on a roller of hard rubber or other insulating material, and the sliding contact is effected by means of a small roller which travels along the wire. All these different forms of apparatus can be obtained from most of the firms which manufacture standard physical apparatus.

Thirdly, additional arbitrary resistances can be introduced at either end or at both ends of the bridge wire. As has already been stated, results are most accurate when the readings are made near the middle of the bridge wire. For this reason it is customary, when additional resistance is introduced, to place equal resistances at each end of the bridge wire. On the supposition, however, that they are unequal, let them be designated by $R_1$ and $R_2$.

and the resistance of the bridge wire by $R$. Then, if the bridge reading is $A$, the ratio $a:b$ is equal to

$$\left(R_1 + R\frac{A}{1000}\right) : \left(R_2 + R\frac{1000-A}{1000}\right),$$

or

$$\left(1000\,\frac{R_1}{R} + A\right) : \left(1000\,\frac{R_2}{R} + 1000-A\right).$$

The total resistance can be made ten times that of the bridge wire by making the two resistances, $R_1$ and $R_2$, equal, and making each one equal to $4.5 \cdot R$. Then the ratio $a:b$ equals

$$(4500 + A) : (4500 + 1000-A),$$

or

$$\left(450 + \frac{A}{10}\right) : \left(1000-(450 + \frac{A}{10})\right).$$

The value of $\frac{a}{b}$ can then be found directly from Obach's tables by using $450 + \frac{A}{10}$ for $a$.

Sometimes it is desirable to measure resistances very much greater than any that can be obtained from the resistance box at hand. In this case, proceeding in the usual way, it is impossible to bring the reading near the middle of the bridge wire. Determinations can, however, be readily made by introducing the extra resistance, referred to above, only at one end of the wire and opposite the resistance to be measured. If $R_1$ is the resistance introduced and it is made equal to $9\,R$, Obach's tables can again be employed, $^1/_{10}\,A$ being used for $a$, provided that the additional resistance was introduced at the right hand of the bridge.

**INDUCTION APPARATUS.**—Alternating currents for conductivity measurements are produced almost exclusively by means of induction coils with a **Neeff's interrupter.** Ostwald recommends a small coil, such as is frequently used with some medical appliances. The tone minimum in the telephone depends to a considerable degree on the nature of the induction apparatus, so if continued difficulty is experienced in obtaining a sharp minimum,

other induction coils should be tried. Sometimes the sharpness is increased by removing the brass tube which sometimes surrounds the core. Filing down the little iron point on the spring frequently increases the rapidity of the vibrations.

Kohlrausch recommends a somewhat larger apparatus having a core of soft iron about 1 cm. in diameter and 8 cm. in length. This is wound with two coils of copper wire, the inner consisting of 200 windings of wire 0.5 mm. in diameter, and the outer of 1000 windings of wire whose diameter is 0.25 mm. A current from one or two Daniell elements or from one accumulator is sufficient to operate it. If the interrupter vibrates against a mercury pole, its point should be of platinum. To prevent its becoming warm, the mercury, in this case, should be in a cup arranged so that water can be kept circulating over it.

Fig. 11.

The so-called **string interrupter** *(Saitenunterbrecher)*, Fig. 11, is sometimes employed. The vibrations of a horizontal steel string, *a b*, under tension, open and close both the primary and secondary circuits. The vibrations are induced by a small electromagnet *m* in the primary circuit. The contacts, as shown in the figure, are commonly between platinum points and mercury. This form of interrupter is especially well adapted for use with the optical telephone or vibrations galvanometer, because the vibrations can be so easily controlled by simply adjusting the tension of the string.

**INSTRUMENTS FOR DETERMINING CURRENT ABSENCE WITH ALTERNATING CURRENTS.**—The telephone is the cheapest and most commonly used of any of the instruments for detecting the absence of current in conductivity determinations with alternating currents. One should be selected which gives a good tone with relatively weak currents. This can only be determined

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satisfactorily by trial. A slight buzzing sound of the interrupter, like the singing of a mosquito, is best adapted to produce a clear tone in the telephone. Under the most favorable conditions one should be able to make the setting correctly to $^1/_{100,000}$, and under ordinary conditions to $^1/_{5000}$ of the length of the bridge wire. A beginner frequently finds it helpful to close one ear with cotton or with a suitable wooden plug. With a little experience, however, one finds no difficulty in distinguishing the sound in the telephone from that of the interrupter.

It is usually impossible to obtain absolute silence in the telephone. The setting is then made by moving the contact slightly backwards and forwards until two points are found, one at the right and the other at the left of the minimum, where the tone is the same. The correct setting is midway between these two points.

Since the source of the current and the current measuring instrument can be interchanged, it is usually advantageous to change the arrangement shown in Fig. 3. The induction apparatus is then in $A\,C$ and connected with the sliding contact, and when the key of the contact is open no current flows through the bridge. When difficulty is experienced in obtaining a clear tone in the telephone, it can be frequently much improved by introducing resistance, if necessary up to several thousand ohms, in the secondary circuit between a pole of the induction apparatus and the sliding contact on the wire. Under such conditions, to avoid statical charging of the telephone or other parts of the apparatus, the other pole of the induction coil should be grounded.

Another instrument which may be used to measure alternating currents is the so-called **optical telephone.** It is more complicated and much more difficult to adjust than a common telephone, but when once adjusted very accurate measurements can be made with it. An outline of the essential features of the apparatus is shown in Fig. 12. A corrugated strip of German silver or of brass foil swings between the poles of two horseshoe magnets, each of which is formed, as in the Bell telephone, by attaching small electromagnets to larger permanent magnets. The poles are arranged, as in the figure, so that one positive and one negative pole are on each side, unlike poles being opposite each other. The current passes through the electromagnets in such a way

that by altering its intensity the magnetism of one of the permanent magnets is increased while that of the other is diminished. On the corrugated metallic filament between the magnets are fastened two circular discs of soft iron. To these discs is attached a brass pin *b*, which transfers the motion of the filament to a mirror *m*, from which a beam of reflected light is thrown on a scale in the observing telescope. A current of $5 \times 10^{-8}$ amperes, under favorable conditions, gives a sensible deflection.

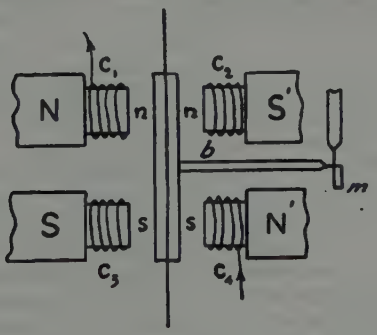



Fig. 12.

A disadvantage of the optical telephone is that it will react only with a current whose period of alternation corresponds to that of the tone of the metallic filament. The string interrupter, page 21, with vibrating metallic string is best adapted for use with this instrument, since it permits an adjustment of the period of alternation of the current within certain limits. The filament of the optical telephone can also be adjusted, so that its tone may be varied within a limited range. When the difference between the period of vibration of the filament and the period of the current is too great to be brought into harmony by either of these means, the filament of the instrument must be replaced by one whose tone corresponds to the alternation period of the current. Four filaments, whose periods of vibration are 64, 128, 256 and 512, will be found sufficient for the adjustment in nearly every

case. Reference is made to the articles of Wien[1] for further particulars as to the apparatus itself and as to the means employed to overcome the effects of overtones.

Other instruments which have been used to measure alternating currents are the **electrodynamometer** and the **vibrations galvanometer**. The former is now but little employed, and the latter is somewhat similar in its construction and use to the optical telephone.[2]

[1] *Wied. Ann.*, 42, 593, and 44, 681 (1891).
[2] See Rubens: *Wied. Ann.*, 56, 27 (1895).

## CHAPTER III.

### Sources of Error with Alternating Currents. Calibration of Bridge Wire.

**HEATING EFFECT OF CURRENT.**—This is a source of error which may have serious consequences if not given sufficient attention, since a difference of temperature of 1° changes the conductivity of a solution on the average about 2 per cent. This can, however, readily be obviated by attending carefully to the following details. The electrolytic vessel should always be kept in a bath of constant temperature (see Chapter IX). The glass walls of the vessel should be thin, so as to permit rapid equalization of temperature. Vessels of unnecessarily great diameter should be avoided, and for very accurate work a thermometer should project directly into the liquid in the cell. Unnecessarily strong currents should not be employed, and the circuit should be closed only for an instant, while the bridge reading is made. This last is best accomplished by arranging the apparatus as has already been suggested, that is, by connecting one pole of the induction coil directly with the sliding contact on the bridge wire.

**SELF-INDUCTION, CAPACITY.**—Resistances up to 1000 ohms can always be determined with considerable accuracy regardless of these influences. Whenever it is desired to work with a greater degree of accuracy or with higher resistances, it is necessary first of all that the chemical preparation of the solution be undertaken with the greatest skill, otherwise further refinements of manipulation will be useless. The above influences, if present, are always self announcing when working with a telephone, because they affect its tone, rendering it difficult to recognize the minimum.

Ordinary non-inductive or differential winding of resistance coils will not commonly prevent self-induction and capacity in coils of over 1000 ohms resistance. Resistances above this limit should be wound either by first twisting the wires together and then proceeding as in the ordinary differential winding,[1] or according to the method of Chaperon,[2] whereby resistance coils are con-

[1] See Price: "*Measurement of Electrical Resistance*," p. 45 (Oxford, 1894).

[2] *Compt. Rend.*, 108, 799 (1889).

structed by winding a single wire alternately forwards and backwards. By these methods resistances up to 100,000 ohms can be constructed, which are practically free from capacity. Graphite lines, page 17, are sometimes used for high resistances for the same reason.

The electrolytic vessel itself sometimes possesses capacity, which seriously affects the tone minimum of the telephone particularly when using liquids of low conductivity. This is caused by the induced charges on the outer wall of the vessel in the bath. It is best overcome by using for the bath a non-conducting liquid, as oil.

When capacity or self-induction exists in some branch of the Wheatstone bridge and cannot readily be removed by other means, the introduction of a condenser of suitable capacity in parallel as compensation frequently removes the difficulty. That branch of the bridge in which the condenser improves the tone minimum is found by trial. The capacity of the condenser is then adjusted until the trouble is removed.

**POLARIZATION.**—This seldom occurs to a sufficient extent to cause inconvenience when using alternating currents. Occasionally, however, in the case of good conductors it produces ill effects. It can then usually be prevented by using large electrodes, which are thoroughly covered with platinum black. It can also be compensated by introducing in a neighboring branch of the bridge a cell provided with small pointed electrodes which lie close together and containing as electrolyte either well conducting sulphuric or hydrochloric acid.[1]

### CALIBRATION OF BRIDGE WIRE.

**METHOD OF STROUHAL AND BARUS.**—A bridge wire is seldom of uniform resistance. It is, therefore, necessary to determine the corrections which must be applied to the bridge readings in order to yield accurate values for the ratio $\frac{a}{b}$. The method of calibration of Strouhal and Barus[2] is a most excellent one for the reason that the corrections obtained are independent of the value of any set of standard resistances. When, however, one possesses

[1] See Nernst: *Zitschr. phys. Chem.*, 14, 622 (1894).
[2] *Wied. Ann.*, 10, 326 (1880).

a reliable set of standard resistances, the method which follows this will be found more rapid and it also involves less calculation.

A number $n$ of equal resistances are made from a suitable kind of wire, as German silver, so that the resistance of a single one is a trifle greater than $1/n$ part of the resistance of the bridge wire. Ten is the number usually chosen. These are soldered to short heavy amalgamated copper wires. These $n$ wires are then

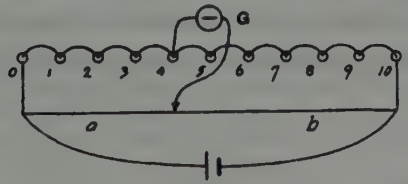



Fig. 13.

connected by means of mercury cups, 0, 1, 2, etc., Fig. 13. The end cups are connected with the bridge terminals by means of heavy amalgamated copper wires. If a direct current is employed, a galvanometer is introduced at $G$; if the current is alternating, a telephone.

The method of calculating the corrections given below is that of Kohlrausch and is more easily intelligible without an example than that originally given by Strouhal and Barus.

One of the $n$ resistances will be distinguished from the others and will be designated by $M$. With this one resistance $M$ each $n$th portion of the bridge wire is to be compared, in the example shown in the figure, where the wire is 1000 mm. long, each 10th portion, that is, from 0 to 100, 100 to 200, etc. This interval, here 100, will be designated by $a$. The resistances of the $n$ such intervals will be indicated by $r_1, r_2, \ldots, r_n$, in order.

$M$ is first placed in the position between cups 0 and 1, and $G$ is connected with cup 1. The reading is found to be $a + \Delta_1$, that is, in this instance $100 + \Delta_1$. $M$ is now exchanged with the next resistance at the right, and with $G$ still connected with 1 the reading is $a + \delta'_2$, with $G$ in 2 the reading is $2a + \delta''_2$. Let $\delta''_2 - \delta_2' = \Delta_2$. $M$ is then exchanged with the next resistance in order, and with $G$ still in cup 2 the reading is $2a + \delta'_3$; with

$G$ in cup 3, it is $3a+\delta_3''$. Let $\delta_3''-\delta_3' = \Delta_3$. $M$ is then exchanged with the next resistance to the right and readings made as before, and so on until M is in the $n$th position, 10th in the figure, where the reading is $(n-1)a+\delta_n'$. Let $-\delta_n' = \Delta_n$.

It is, therefore, clear that each of the $n$ intervals, $r_1+\Delta_1, r_2+\Delta_2, \cdots r_n+\Delta_n$, has the same resistance, which will be called $r$. If $R$ is the total resistance of the bridge wire, then

$$R = r_1 + r_2 + \cdots + r_n = nr - \Delta_1 - \Delta_2 - \cdots - \Delta_n.$$

Let $\frac{\Delta_1 + \Delta_2 + \cdots + \Delta_n}{n} = \alpha$, consequently $r = \frac{R}{n} + \alpha$,

and

$$r_1 = \frac{R}{n} + \alpha - \Delta_1,$$

$$r_2 = \frac{R}{n} + \alpha - \Delta_2,$$

$$\cdots\cdots\cdots\cdots\cdots$$

$$r_n = \frac{R}{n} + \alpha - \Delta_n.$$

Remembering that $\frac{R}{n} = a$, the corrections for readings at $a$, $2a$, $\cdots$ $(n-1)a$, are therefore,

| Reading. | Correction. |
|---|---|
| $a$ | $\alpha - \Delta_1$ |
| $2a$ | $2\alpha - \Delta_1 - \Delta_2$ |
| $3a$ | $3\alpha - \Delta_1 - \Delta_2 - \Delta_3$ |
| .. | ..... |
| $(n-1)a$ | $(n-1)\alpha - \Delta_1 - \Delta_2 \cdots - \Delta_n$. |

The above include not only corrections for inequalities of resistance in the bridge wire, but also for any resistances at the points of contact or for any displacement of the 0 or 1000 point. The actual corrections at 0 and 1000 can only be obtained by extrapolation, and the extrapolated values are, of course, more nearly correct the greater the value of $n$.

**CALIBRATION BY MEANS OF A SET OF RESISTANCES.**—For calibrating a bridge wire either one set or two sets of resistances may be employed. The separate resistances should be accurate, or at least should be provided with a table of corrections. The

method when only one set of resistances is employed will be described, and the modification necessary when two sets are employed will readily suggest itself from it.

The apparatus is arranged as in Fig. 3, except that in place of $S$ and $R$ are introduced two suitable resistances of the resistance box, which will be designated as $R_a$ and $R_b$. The reading on the bridge wire, under these conditions, should be $a = \frac{R_a}{R_a + R_b} L$, where $L$ is the length of the wire, usually 1000 mm. Many pairs of resistances can be found in most resistance sets, so that the possible positions on the bridge wire are numerous enough for complete calibration. A few such combinations, commonly found in standard resistance sets, are given below.

| Rheostat. | | | | Bridge. | |
|---|---|---|---|---|---|
| $R_a$, Ohms | $R_b$, Ohms | or $R_a$, Ohms | $R_b$, Ohms | $a$. | $b$. |
| 5 | 495 | 10 | 990 | 10 | 990 |
| 10 | 190 | 50 | 950 | 50 | 950 |
| 50 | 450 | 100 | 900 | 100 | 900 |
| 30 | 170 | 150 | 850 | 150 | 850 |
| 50 | 200 | 100 | 400 | 200 | 800 |
| 50 | 150 | 100 | 300 | 250 | 750 |
| 150 | 350 | 300 | 700 | 300 | 700 |
| 70 | 130 | 350 | 650 | 350 | 650 |
| 100 | 150 | 200 | 300 | 400 | 600 |
| 90 | 110 | 450 | 550 | 450 | 550 |
| 100 | 100 | 200 | 200 | 500 | 500 |

To calibrate beyond the middle of the bridge, $R_a$ and $R_b$ are simply reversed, that is, $R_b$ is introduced opposite the lower end of the bridge, and then the same pairs of resistances can be used.

In case the separate resistances of the rheostat are so accurate that no corrections need be applied, the corrections for the bridge wire can be obtained very simply. If $a$ is the actual reading found and $a_1$ is what it should be from the equation $a_1 = \frac{R_a}{R_a + R_b} L$, then the correction at this point is $a_1 - a$. On the other hand, in case the corrections to the separate resistances are too large to neglect, the calculation is more complicated, but can be obtained by first correcting the resistances $R_a$ and $R_b$ and then proceeding as before.

**DIMINISHING AND CONTROLLING CORRECTIONS.**—If the corrections for one-half of the bridge wire are positive and for the other half negative, and they amount to 1 mm. or more, it is advisable to diminish them by displacing the contacts of the wire at each end, a short distance toward the middle of the bridge. When the corrections at one end are much greater than at the other end, a displacement only at the end requiring the greater corrections is frequently all that is necessary.

The resistance of the bridge wire may undergo a change with the time, consequently the calibration should be occasionally verified. Most subject to change are the resistances at the points of contact at the ends of the bridge. According to Kohlrausch this last change can be readily detected by comparing two resistances of very different value, introduced at $S$ and $R$, Fig. 3, first with the bridge wire alone, and, secondly, with the bridge wire plus nine times its resistance ($9R$, see page 20). Both readings are corrected according to the table derived from a former calibration. These corrected readings will be designated by $a$ and $A$. If the corrections applied were accurate, and the smaller resistance was opposite the left end of the bridge, then $A$ should equal $10a$. Otherwise the imaginary zero-point has been displaced, and the former correction at o is to be increased by $e_0 = \frac{1}{9}\left(A - 10a.\right)$ If the smaller resistance was opposite the right end of the bridge, then $A$ should equal $10a - 9000$. If this is not so, the correction at 1000 is to be increased by $e_1 = \frac{1}{9}\left(A + 9000 - 10a.\right)$ For the above equations to be strictly correct, $a$ must lie very near one end of the bridge or the other, that is, the greater resistance compared should be at least 100 times the smaller. The former correction for any reading $a$ is then to be increased by

$$\frac{1}{1000}\left(ae_1 + (1000 - a)e_0\right),$$

or more simply by

$$e_0 + \frac{a}{1000}\left(e_1 - e_0\right).$$

Let us suppose, for example, a series of corrections, of which

the one at $0 = +0.8$, at $1000 = -0.2$, and the intermediate ones lie between these values. In order to make the corrections smaller, the end contact on the left is displaced slightly toward the middle of the bridge. The end corrections are now found by the above process to be at $0 + 0.1$, at $1000 - 0.2$,
while formerly they were at $0 + 0.8$, at $1000 - 0.2$,
Therefore $e_0 = -0.7$, and $e_1 = \pm 0.0$.
The former correction for any reading, $a$, must now be changed by the value, $e_0 + \frac{a}{1000}\left(e_1 - e_0\right) = -0.7 + 0.0007a$. At 400, for instance, the correction must be changed by $-0.7 + 0.28 = -0.4$.

For the most accurate work a table of corrections should be carried to the second decimal place. This is to be accomplished by making several observations at each point while calibrating and taking the average.

## CHAPTER IV.

### Determination of Resistance Capacity.

**DIRECT METHOD BY MEASUREMENT OF CELL.**—This method depends upon the measurement of the dimensions of the electrolytic vessel. A vessel of cylindrical form, whose dimensions can be accurately determined and the electrodes of which entirely fill the cross-section, is best adapted to this purpose.

It has been already shown, in the first chapter, that $C = \frac{l}{s}$, where $l$ is the length of the column of solution between the electrodes in centimeters and $s$ is the area of a cross-section in square centimeters. If $v$ is the volume between the electrodes in cubic centimeters, which can be determined very accurately by calibrating with mercury or water, then the formula may be written $C = \frac{l^2}{v}$. This gives the capacity very readily on the hypothesis that the lines of force are everywhere parallel to the axis of the cylinder. The calculation is illustrated in connection with Stroud and Henderson's method for the determination of conductivity in Chapter I. Mercury should always be used for determining the volume $v$ when the electrolytic vessel is small. For further details reference is made to the work of Kohlrausch, Holborn and Diesselhorst,[1] who have determined the conductivity of most of the standard solutions mentioned in this Chapter.

**INDIRECT METHOD, BY THE KNOWN CONDUCTIVITY OF STANDARD SOLUTIONS.**—This method is the one almost exclusively employed for practical work, since it is much more rapid than the direct method, and since the latter requires much greater skill in manipulation. The conductivities of a sufficient number of standard solutions are known to render a determination of the resistance capacity of any vessel within the limits commonly required a comparatively simple matter.

It has already been shown that $C = \kappa R$; therefore, when $\kappa$ is known for any solution, $C$ can be found at once by measuring the resistance $R$ of the solution in the vessel whose resistance ca-

[1] *Wied. Ann.*, 64, 423 (1898).

pacity is sought. To render the method as accurate and as rapid as possible, the standard solutions of known conductivity should be of such a nature that they can be accurately reproduced without great effort. For this reason solutions of maximum conductivity have been chosen for low resistances. The conductivity of such solutions changes but little with slight changes of concentration, and they can, therefore, be prepared sufficiently accurately from specific gravity determinations. For standard solutions of high resistance dilute solutions of potassium chloride are usually employed. This salt is quite stable in the air, and can also be purified without great difficulty. A saturated solution of calcium sulphate is sometimes employed instead of dilute solutions of potassium chloride. Detailed directions for the preparation of the different solutions follow.

**Sulphuric Acid of Maximum Conductivity.**—Thirty per cent. $H_2SO_4$; specific gravity, 18°, = 1.223. Ordinary chemically pure sulphuric acid answers the purpose. The solution can be prepared with sufficient accuracy by determination of the specific gravity by means of a hydrometer (of course, one which is known to be accurate).

**Magnesium Sulphate Solution of Maximum Conductivity.**—17.4 per cent. $MgSO_4$; specific gravity, 18°, = 1.190; 424 grams $MgSO_4 + 7H_2O$ made up to 1 liter. The chemically pure salt should be recrystallized once. After the solution has been prepared it should be checked by a determination of the specific gravity with the hydrometer.

**Saturated Solution of Sodium Chloride.**—One liter of water dissolves 360 grams NaCl, which quantity is but little influenced by changes of temperature. Chemically pure NaCl which has been heated to low redness gives good results. Care should be taken to have the solution completely saturated. It should be prepared at a high temperature with an excess of the salt. The last portions of salt added should be very finely pulverized, and the addition should be accompanied by thorough shaking

**Normal Potassium Chloride Solution.**—74.59 grams KCl in 1 liter solution at 18°; if weighed in air, 74.555 grams. Specific gravity, 18,° = 1.04492. The weighing should be conducted with all possible care, as a determination of the specific gravity is of little

value as a control unless made with the greatest accuracy. A difference in the specific gravity of a unit in the fourth decimal place causes an error of 0.2 per cent. The chemically pure salt should be recrystallized once or twice and then heated to low redness for a short time.

**More Dilute Solutions of Potassium Chloride.**—Decinormal solution contains 7.4555 grams KCl weighed in air in 1 liter at 18°, or 100 cc. of the normal solution is diluted to 1 liter.

Fiftieth-normal solution of potassium chloride is prepared by making 1.4910 grams KCl up to 1 liter at 18°, or by diluting 20 cc. normal or 200 cc. decinormal solution to 1 liter.

Hundredth-normal potassium chloride solution, prepared similarly, is also sometimes employed.

**Saturated Solution of Calcium Sulphate.**—This possesses the advantage of requiring no weighing. The following method of preparation, suggested by Hulett and Allen,[1] insures a solution of very constant conductivity. Hulett[2] has shown that the saturation of a solution depends on the size and form of the solid with which it is in contact. He found that the solubility of gypsum increased 20 per cent. by decreasing the size of the solid particles to 0.3 micron. A solution of constant content cannot, therefore, be prepared by rotating gypsum with water, because some of the particles become smaller from abrasion.[3] To insure a solution of constant content pure water must be rotated carefully above plates of gypsum of from 0.5 to 1.0 mm. thickness, which lie on the bottom of a flask in a bath of constant temperature. The solution is best removed from the saturating flask to the conductivity vessel by means of a pipette. Proceeding according to this method the conductivity was found to be constant at 25° after seventy-five minutes, unless the solution had become supersaturated. In this case a much longer time, frequently two days, was required. At 18° a saturated solution contains 2.016 grams $CaSO_4$ in 1 liter; at 25°, 2.081 grams.

**Use and Conductivity of the Standard Solutions.**—Distilled water

[1] *J. Am. Chem. Soc.*, 24, 667 (1902).

[2] *Ztschr. phys. Chem.*, 37, 385 (1901).

[3] Kohlrausch: *Ztschr. phys. Chem.*, 44, 197 (1903), and Böttger: *Ibid.*, 46, 546 (1903), have, however, obtained solutions of this salt of practically constant content by shaking the finely pulverized material with water, the first few washings being rejected.

should be used in preparing all of the above solutions. For the more dilute solutions of potassium chloride and for the calcium sulphate solution only specially purified distilled water (see next chapter), possessing a specific conductivity not greater than $1.5 \times 10^{-6}$, should be used. Furthermore, the solutions should be made up, if possible, only just before using. If, however, it seems necessary to preserve any of them for several days, it should be done only in well stoppered bottles of good glass, which have previously been exposed to prolonged contact with aqueous solutions.

Which one of the solutions is to be used to determine the resistance capacity of a vessel depends on the approximate value of such capacity. If resistances of from 50 to 2000 ohms can be readily employed, the following table gives the limits of the capacities for the determination of which the different solutions are best adapted:

| Solution. | Resistance capacity. | |
|---|---|---|
| $H_2SO_4$, maximum conductivity | 40 to | 1500 |
| NaCl, saturated | 10 | 400 |
| KCl, normal | 5 | 200 |
| $MgSO_4$, maximum conductivity | 3 | 100 |
| KCl, decinormal | 0.5 | 20 |
| KCl, fiftieth-normal | 0.1 | 4 |
| Gypsum, saturated | 0.1 | 4 |
| KCl, hundredth-normal | 0.05 | 2 |

The table below gives the specific conductivity of these solutions for temperatures from 15° to 25°. The solutions of NaCl

SPECIFIC CONDUCTIVITY OF STANDARD SOLUTIONS.

| Temperature. | $H_2SO_4$ (max.). | NaCl (saturated). | $MgSO_4$ (max.). | KCl (normal). | KCl (N/10). | KCl (N/50). | KCl (N/100). | Gypsum (saturated). |
|---|---|---|---|---|---|---|---|---|
| 15° | 0.7028 | 0.2015 | 0.04555 | 0.09252 | 0.01048 | 0.002243 | 0.001147 | 0.001736 |
| 16 | 0.7151 | 0.2063 | 0.04676 | 0.09441 | 0.01072 | 0.002294 | 0.001173 | 0.001774 |
| 17 | 0.7275 | 0.2112 | 0.04799 | 0.09631 | 0.01095 | 0.002345 | 0.001199 | 0.001833 |
| 18 | 0.7398 | 0.2161 | 0.04922 | 0.09822 | 0.01119 | 0.002397 | 0.001225 | 0.001881 |
| 19 | 0.7522 | 0.2210 | 0.05046 | 0.10014 | 0.01143 | 0.002449 | 0.001251 | 0.001928 |
| 20 | 0.7645 | 0.2260 | 0.05171 | 0.10207 | 0.01167 | 0.002501 | 0.001278 | 0.001976 |
| 21 | 0.7768 | 0.2310 | 0.05297 | 0.10400 | 0.01191 | 0.002553 | 0.001305 | 0.002024 |
| 22 | 0.7890 | 0.2360 | 0.05424 | 0.10594 | 0.01215 | 0.002606 | 0.001332 | 0.002070 |
| 23 | 0.8013 | 0.2411 | 0.05551 | 0.10789 | 0.01239 | 0.002659 | 0.001359 | 0.002116 |
| 24 | 0.8135 | 0.2462 | 0.05679 | 0.10984 | 0.01264 | 0.002712 | 0.001386 | 0.002161 |
| 25 | 0.8257 | 0.2513 | 0.05808 | 0.11180 | 0.01288 | 0.002765 | 0.001413 | 0.002208 |

and gypsum were saturated at the temperature for which the conductivity is given.[1]

When determining large resistance capacities it is best to employ magnesium sulphate of maximum conductivity, if possible, on account of the probability of error being less than with any of the other solutions. An error of 0.003 in determining the specific gravity of this solution only produces a change in the conductivity of a single unit in the last decimal place.

**SECOND INDIRECT METHOD, BY COMPARISON WITH THE KNOWN RESISTANCE CAPACITY OF A SECOND VESSEL.**—Both the vessel of known capacity and the one whose capacity is to be determined are filled with the same solution and placed in the same temperature bath. The resistances of the two are then measured. These will be designated by $R$ and $R_1$, and the corresponding capacities by $C$ and $C_1$. Since the capacities of the vessels are in the same ratio as the measured resistances, and the conductivities are, of course, equal,

$$\frac{C}{C_1} = \frac{R}{R_1}.$$

From this the value of $C$ can be readily obtained. When the greatest accuracy is desired the resistances $r$ and $r_1$ of the conducting wires must be considered, in which case

$$\frac{C}{C_1} = \frac{R-r}{R_1-r_1}.$$

For determining large resistance capacities solutions of potassium hydrogen sulphate are commonly employed, while for determining the smaller ones a boric acid-mannit solution is preferable. These solutions possess a conductivity which varies but little with the temperature. The boric acid-mannit solution is prepared by dissolving 121 grams mannit, 41 grams boric acid and 0.06 gram potassium chloride in water and making up to a total volume of 1 liter at 18°. At this temperature the specific conductivity of the solution is 0.00097.

The accuracy of this method is greater the nearer the value of the known capacity is to that of the unknown.

[1] The figures in the above table are all taken from Kohlrausch, Holborn, and Diesselhorst: *Wied. Ann.*, 64, 440 and 451 (1898), except those for gypsum, which are the values given by Hulett: *Ztschr. phys. Chem.*, 42, 577 (1903).

Whatever the method used for determining the resistance capacity of a vessel, attention should be given to the following point. When the electrodes of a vessel stand vertically (Fig. 4, *a*, Fig. 5, *b* and *c*), the resistance capacity must be determined for a definite filling, that is, either for a certain volume or up to a mark on the glass. Then, whenever the vessel is used the liquid should stand at the same height, otherwise the capacity will be different from that determined. Vessels of the Arrhenius form with the electrodes horizontal (Fig. 5, *a*) possess a constant resistance capacity, no matter how much solution is used, provided the electrodes are covered in every instance.[1]

**CALIBRATION OF A VESSEL FOR VARIABLE RESISTANCE CAPACITY.**—It is frequently desirable to possess a vessel whose

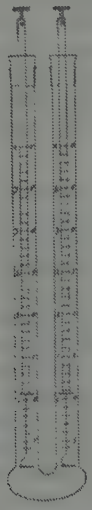


Fig. 14.

resistance capacity can be readily varied. Such vessels are commonly of the U-tube form, as shown in Fig. 14. The electrodes,

[1] *J. Phys. Chem.*, 6, 557 (1902).

one of which is in each limb, are capable of being raised or lowered. The calibration is accomplished by filling the tube with one of the standard solutions best adapted to the range of capacities which it is wished to determine, for instance, tenth-normal potassium chloride. First a position of the electrodes is sought, where, being at the same height, they yield some simple value for the capacity, as 1. $\kappa = 0.01119$ for tenth-normal KCl at 18°. The resistance, therefore, under the above conditions is $\frac{C_1}{0.01119} = \frac{1}{0.01119} = 89.4$ ohms. Consequently a resistance of 89.4 ohms is introduced, and both electrodes are raised or lowered together until the resistance of the solution exactly equals this. If it is difficult with the apparatus at hand to introduce fractions of an ohm, the necessity for it can be overcome by properly changing the temperature. For example, in this case the temperature of the bath can be set at 23.44°, at which temperature $\kappa = 0.01250$ for tenth-normal KCl. The required resistance is then 80 ohms. The position of the electrodes thus determined is marked 0.5 on each limb of the tube.

One only of the electrodes is then raised until the resistance is one and a half times 89.4 ohms at 18°, or one and a half times 80 at 23.44°. This new position is marked 1. The second electrode is then raised until the resistance is twice its first value and the position on this limb marked 1. This procedure is continued until the desired number of calibrations have been made. For any setting of the electrodes the resistance capacity is given by simply adding together the numbers on each limb against which the electrodes are set. For instance, if one electrode stands at the mark 1.5 in one limb and the second electrode at the mark 2.5 in the other limb the resistance capacity is then 4. Of course, conductivities depending on resistance capacities obtained in this way are by no means as accurate as those depending on the resistance capacity of a vessel in which the electrodes have an invariable position.

If the bore of the tube is uniform the calibration can be made

by the direct method in each of the vertical limbs, after the capacity has been determined for the bent portion by means of a solution of known conductivity, as above. That is, after the first positions of the electrodes in each limb, marked 0.5 on the above tube, have been determined, the remainder of the calibration can be made, when the diameter of the tube is known, by laying off the proper lengths from the line marked 0.5, according to the formula, $l = Cs$ (page 4).

## CHAPTER V.

### Water. Preparation of Solutions.

**CONDUCTIVITY OF WATER.**—The conductivity of ordinary water is quite considerable owing to the impurities which it contains. After a single distillation the conductivity is usually reduced to from 3 to $6 \times 10^{-6}$. By distilling with special care the conductivity can be brought as low as 0.7, or $0.8 \times 10^{-6}$. The purest water whose conductivity has ever been measured, is probably that prepared by Kohlrausch and Heydweiller[1] by redistilling *in vacuo* water which was already as pure as could be obtained in contact with air. The glass apparatus used by them for this purpose had been in contact with water for ten years, and, therefore, was very resistant to the further action of this liquid.

The specific conductivity of this pure water at 18° is given by Kohlrausch and Heydweiller in reciprocal Siemens units as $0.0404 \times 10^{-10}$. From their results the conductivity has been calculated at 0°, 18°, 25°, 35° and 50° in reciprocal ohms, and the values so obtained are given in the table below in the column Obs. These investigators also estimated the temperature coefficient of the conductivity of pure water according to the principles of the dissociation theory. Combining this with their most probable value for the conductivity of water at 18° and estimating the effect of the impurities still present, they derive a theoretical expression for the conductivity of pure water at any temperature $t$, which, recalculated to reciprocal ohms, is as follows:

$$10^6 \kappa = 0.03586 \times 10^{-\frac{2275}{(273+t)}} \times (319 + 7.5t).$$

From this the values in the column Theoret. are calculated.

| | Specific conductivity. | |
|---|---|---|
| Temperature. | Obs.[2] | Theoret. |
| 0° | $0.016 \times 10^{-6}$ | $0.012 \times 10^{-6}$ |
| 18 | $0.043 \times 10^{-6}$ | $0.038 \times 10^{-6}$ |
| 25 | $0.063 \times 10^{-6}$ | $0.058 \times 10^{-6}$ |
| 35 | $0.100 \times 10^{-6}$ | $0.094 \times 10^{-6}$ |
| 50 | $0.190 \times 10^{-6}$ | $0.183 \times 10^{-6}$ |

[1] *Wied. Ann.*, 53, 209 (1894).

[2] These numbers are based on the value $0.0404 \times 10^{-10}$ at 18° and on results obtained by Kohlrausch and Heydweiller on January 28 and February 14; *loc. cit.*, p. 227.

The conductivity of water is seen to vary greatly with the temperature, which is in accord with the principles of thermodynamics. In round numbers the conductivity of pure water at 18° may be taken as $0.04 \times 10^{-6}$, about ten times less than that of any water in contact with the air.

**PURIFICATION OF WATER.**—By a single distillation the conductivity of water, as has been said, is usually reduced to from 3 to $6 \times 10^{-6}$. In preparing solutions for conductivity determinations water of this degree of purity should be used only when the conductivity of the solution has a considerable value, that is, exceeds 0.001. For the preparation of solutions whose conductivity is less than this, distilled water must be still further purified

Hulett[1] recommends distilling water twice, once from an acid solution and the second time from an alkaline solution. Before the first distillation 5 cc. each of sulphuric acid and of a concentrated solution of potassium dichromate (or permanganate) are added to each liter of water. This distillate is then made alkaline with baryta water, 25 cc. to a liter, and distilled again. Hulett used a condenser of platinum, which was thrust well up into the neck of the retort, so that only the water condensing in the platinum tube would run into the receiver. A condenser of silver, block tin or even a good quality of glass may replace the platinum without materially affecting the result.

Jones and Mackay[2] have also described a method for purifying water very similar to the above. The two distillations are, however, continuous, the distillate from the first being collected in a retort from which it is at once distilled into a permanent receiving flask. The second retort contains, instead of baryta water, an alkaline solution of potassium permanganate. Water can be obtained by these methods which has a conductivity as low as $0.8 \times 10^{-6}$.

In a recent article Kohlrausch[3] suggests several means by which the conductivity of water may be greatly reduced. He found that the conductivity of distilled water diminished by simply standing in contact with platinized electrodes, presumably on account of

[1] *Ztschr. phys. Chem.*, 22, 397 (1896), and *J. Phys. Chem.*, 1, 91 (1896).
[2] *Am. Chem. J.*, 19, 90 (1897).
[3] *Ztschr. phys. Chem.*, 42, 193 (1902).

the oxidation of traces of ammonia. By allowing a rapid current of $CO_2$-free air to pass through water in the conductivity vessel, where it was also in contact with the electrodes, the conductivity was reduced to $0.28 \times 10^{-6}$, the lowest value yet obtained for the conductivity of water in contact with the atmosphere.

The removal of $CO_2$ from water by aeration in order to improve its conductivity has been frequently practised. The conductivity of water which has been only once distilled, may be greatly reduced by this method. $CO_2$-free air is commonly obtained by passing out-door air through a long tube filled with moist soda-lime or through a concentrated solution of caustic potash. In either case the air should afterwards be passed through a washing bottle, containing distilled water, before it reaches the water to be purified.

Walker and Cormack[1] describe a very efficient method for purifying water. They first distil from an alkaline solution, then this distillate is acidified with phosphoric acid and redistilled, and finally it is distilled a third time without the addition of any chemical. Water treated in this way was found to possess a conductivity of $0.7 \times 10^{-6}$. From the partial pressure of $CO_2$ in the atmosphere they have calculated that the conductivity of water, distilled in contact with air, should be about $0.65 \times 10^{-6}$ on account of this impurity alone. This affords an explanation of the improvement in the conductivity of water when $CO_2$ is re-removed.

Water can also be quite efficiently purified by freezing. A clean flask, containing the water to be purified, is placed in a freezing mixture (salt and ice) whose temperature is about $-10°$. When about one-half of the water has frozen around the inner surface of the flask, the remainder, which contains most of the impurities, is poured off. By treating water which had been once distilled in this way, Nernst was able to reduce the conductivity to $2 \times 10^{-6}$. Kohlrausch and Heydweiller found the same value for the conductivity of a sample of water which was obtained from a piece of natural ice. The conductivity of this water, before freezing, was probably fully 150 times greater than $2 \times 10^{-6}$.

[1] *J. Chem. Soc.* 77, 8 (1901).

**INFLUENCE OF THE SOLUBILITY OF GLASS ON THE CONDUCTIVITY OF WATER.**—Electrolytic vessels and all flasks and bottles used in handling pure water or very dilute solutions should be of a good quality of glass, quite resistant to the solvent action of water.[1] Glass vessels should be boiled out with water or steamed out[2] prior to use. The longer a vessel has been in contact with water, provided it is of good glass, the more resistant is it to the action of water and consequently better adapted to employment for conductivity work. The higher the temperature of water the greater is its effect upon glass.[3] Some glass, no matter how long it is treated with water or steam, is never fit for uses of this kind. The solubility of the glass of any vessel can be tested by determining, from day to day, the conductivity of water allowed to stand in it. This may be done either directly in the vessel itself by means of dip electrodes, or in an electrolytic cell by carefully transferring some of the water with a pipette. If the glass is of good quality the conductivity per 100 cc. water should not increase more than $1 \times 10^{-6}$ in a week.

## PREPARATION OF SOLUTIONS.

**BY WEIGHING.**—The preparation of solutions for conductivity determinations requires great care in order that the error, introduced by inaccuracies of concentration, may not exceed the errors involved in the measurement of the conductivity. This has been frequently overlooked.

A solution of known strength is, if the substance is of a nature to permit it, always best prepared by weighing. All weighing should be reduced to weight *in vacuo* in order to be on a uniform basis. This is readily accomplished by means of the following equation:

$$M = m\left(1 + \frac{\lambda}{s} - \frac{\delta}{s}\right),$$

in which the letters have the following significance:

[1] Kohlrausch: *Wied. Ann.*, 44, 577 (1891); Kohlrausch and Heydweiller: *Wied. Ann.* 53, 210 (1894).

[2] Ostwald and Luther: *Physiko-chemische Messungen*, p. 403.

[3] Schaller: *Ztschr. phys. Chem.*, 28, 497 (1898).

$m$ is the apparent weight in air, that is, the weights which balance the object;

$\lambda$ is the density of air, 0.0012 on an average;

$s$ is the specific gravity of the substance weighed;

$\delta$ is the specific gravity of the weights, 8.4, if brass.

Having thus weighed the proper quantity of the substance, the solution is made up in a graduated flask. The water used for making the solution must be at the temperature for which the flask was graduated.

**BY DETERMINING SPECIFIC GRAVITY.**—Specific gravity determinations should never be substituted for direct weighing, except in preparing concentrated solutions where the specific gravity differs considerably from unity, or in the case of hygroscopic substances which cannot be weighed accurately in the air. In this latter case, if the specific gravity lies near 1, it must be determined with exceptional care. For this purpose an Ostwald-Sprengel pycnometer[1] or a Gay-Lussac specific gravity bottle is capable of yielding accurate results when used in a constant temperature-bath. The following equations are used to reduce specific gravity determined at 15° or 18°, relative to water at the same temperature to that compared with water at 4°:

$$S_{\frac{15}{15}} = 1.00087\, S_{\frac{15}{4}} \cdot \quad S_{\frac{18}{18}} = 1.00138\, S_{\frac{18}{4}}.$$

**BY ANALYSIS.**—If it is desired to determine the strength of a solution which has already been prepared, recourse must be taken to the analytical method. This method is also particularly well suited to the case of solutions prepared from hygroscopic substances. A known volume of the solution is removed by means of a pipette (graduated to hold, not to discharge), the pipette is rinsed out and the analysis made by evaporation or precipitation, according to the nature of the substance.

**GRADUATED FLASKS AND PIPETTES.**—All measuring instruments of glass, designed for accurate work, should be calibrated before being used, for reliance cannot be placed on the indicated capacity. Pipettes designed for discharging are usually calibrated by means of water at known temperature. The water dis-

[1] See Ostwald and Luther: *Physico-chemische Messungen*, p. 142.

charged from the pipette is weighed in a suitable vessel, and to insure as nearly uniform conditions as possible the mouth of the pipette is held against the side of the vessel for a definite length of time, usually fifteen seconds, after free outflow has ceased. (Whenever the pipette is afterwards used care should be taken that it be allowed to discharge precisely the same length of time.) The weight of water thus discharged will be called $m$ grams. This is the weight of water in air. The true volume of the pipette is given by the equation,

$$V_t = m(1 + R) \text{ cc.},$$

in which the value of $R$ is taken from the table below. If the pipette is small, calibrating with mercury is more accurate. In this case the volume is obtained according to the equation,

$$V_t = mR' \text{ cc.}$$

The value of $R'$ is likewise given in the accompanying table.

TABLE COMPILED FROM DATA BY LANDOLT AND BÖRNSTEIN FOR OBTAINING TRUE VOLUME, BASED ON 0.000025 AS THE CUBICAL COEFFICIENT OF EXPANSION OF GLASS.

| $t$. | $R$. | $R'$. | $t$. | $R$. | $R'$. | $t$. | $R$. | $R'$. |
|---|---|---|---|---|---|---|---|---|
| 0° | 0.00164 | 0.073583 | 10° | 0.00153 | 0.073698 | 20° | 0.00278 | 0.073813 |
| 1 | 0.00156 | 0.073595 | 11 | 0.00160 | 0.073710 | 21 | 0.00297 | 0.073825 |
| 2 | 0.00150 | 0.073606 | 12 | 0.00169 | 0.073721 | 22 | 0.00317 | 0.073836 |
| 3 | 0.00145 | 0.073618 | 13 | 0.00178 | 0.073733 | 23 | 0.00338 | 0.073848 |
| 4 | 0.00142 | 0.073629 | 14 | 0.00189 | 0.073744 | 24 | 0.00360 | 0.073860 |
| 5 | 0.00140 | 0.073652 | 15 | 0.00201 | 0.073756 | 25 | 0.00383 | 0.073871 |
| 6 | 0.00140 | 0.073652 | 16 | 0.00214 | 0.073767 | 26 | 0.00407 | 0.073882 |
| 7 | 0.00141 | 0.073664 | 17 | 0.00229 | 0.073779 | 27 | 0.00431 | 0.073894 |
| 8 | 0.00143 | 0.073675 | 18 | 0.00244 | 0.073790 | 28 | 0.00457 | 0.073905 |
| 9 | 0.00147 | 0.073687 | 19 | 0.00260 | 0.073802 | 29 | 0.00484 | 0.073917 |
| | | | | | | 30 | 0.00512 | 0.073928 |

If the pipette is to be calibrated to hold, that is, for volume, the dry pipette and the weighing vessel are first weighed together. The pipette is then filled to the mark with water. This is discharged into the weighing vessel, and the vessel and wet pipette weighed. The difference is the quantity $m$, and the true volume is calculated according to the same equation as above.

Graduated flasks are calibrated by weighing them first empty and afterwards with water up to the mark. The difference is

the quantity $m$ and the true volume can be calculated as before. A liter flask holds 997.667 grams water at 18° when weighed in air.

**DILUTION.**—It is frequently desirable to measure the conductivity of a solution at many different concentrations. When determining the equivalent conductivity of dilute solutions, concentrations frequently employed are $\frac{1}{2}$, $\frac{1}{4}$, $\frac{1}{8}$, $\frac{1}{16}$, etc., normal. Solutions of such strengths can be conveniently obtained by starting with the strongest solution and diluting successively by means of pipettes. To accomplish this a definite volume of solution is taken which well covers the electrodes, for example, 40 cc. After the conductivity has been measured, 20 cc. of the solution are removed with a pipette and a like quantity of water added. The concentration is now one-half its former value. The conductivity is then measured at the new concentration, after which the solution is diluted as before, and this continued until all the desired concentrations have been obtained.

To be especially considered, however, is the fact that a pipette never removes the same volume of liquid that it delivers. Moreover, the use of the same pipette for removing the solution and for adding the water is not advisable, as the water is apt to become slightly contaminated. Two pipettes should, therefore, be employed, one graduated to remove 20 cc., the other graduated to deliver the same amount. Since about five minutes are required to dilute the solution and to measure carefully the conductivity, in calibrating the first pipette allowance should be made for this. It is accomplished by filling the pipette with water, letting run out, and then, after standing on a piece of clean filter-paper for five minutes, drawing up just 20 cc. water from a weighing vessel and marking the height of the liquid on the pipette tube. This should be repeated until one is certain that the correct height has been determined. This height can then be indicated by a permanent mark etched in the glass.

If the electrolytic vessel is small and 20 cc. of solution cover the electrodes, 10 cc. pipettes, properly graduated, are the most suitable to use.

Another method of dilution, which is sometimes employed, is to start with a known volume of water, to which is added, after

each determination of the conductivity, a very small quantity of a strong solution of the substance under investigation whose concentration is known. In this way the solution becomes gradually more concentrated, but the concentrations cannot be expressed by so simple numbers as in the former method. By plotting a curve of the conductivity, however, as found at any concentration (see Chapter VIII), the conductivity at simpler concentrations can be readily estimated.

Neither of the above methods should be used when the greatest accuracy is desired. In this case a solution of each concentration required must be prepared in graduated flasks. The most concentrated solution desired is first made up by weighing, or by whatever method is best suited to the nature of the substance under invesigation. The more dilute concentrations can then be prepared by diluting a suitable aliquot portion of this solution in a graduated flask. Solutions of the concentrations $^1/_2$, $^1/_5$, $^1/_{10}$, $^1/_{20}$, $^1/_{50}$, etc., normal, which are very frequently employed, can be obtained in this way quite easily from a normal solution.

**INFLUENCE OF THE IMPURITIES OF WATER.**—What degree of purity is desirable in water which is to be employed in preparing solutions depends on the conductivity of the solution and has already been sufficiently considered. Water of a specific conductivity of 1 or $2\times10^{-6}$ begins to affect the conductivity of solutions whose concentration has been carried as low as $^1/_{1000}$-normal, and at still lower concentrations the effect is correspondingly more marked. It is, however, frequently necessary to determine the conductivity of solutions considerably more dilute than this in which case, of course, the conductiyity of the water should be considered, and allowance made for it if possible.

In the case of most salts, which react neutral, the correct value is approximated by subtracting from the specific conductivity of the solution that of the water. If this is not done the results are, in many instances, manifestly inaccurate. In the case of acids, bases, and basic reacting salts, the conductivity of the water seems to exercise a much greater disturbing effect, frequently causing a decrease of the equivalent conductivity at great dilutions. When the water has been very efficiently purified, this seems to be due

to the influence of the carbon dioxide of the air. Merely subtracting the conductivity of the water employed by no means suffices as a correction in such cases. The equivalent conductivity, at low concentrations, of substances of this class, which are sometimes given in tables in connection with the conductivity at other concentrations, are very often extrapolated values. Whether this is the case or they are the results of actual measurements, their accuracy is questionable.[1]

[1] For further consideration of this subject see the following: Arrhenius: *Bihang. Svenska Akad.*, 8, Nos. 13 and 14 (1884); Kohlrausch: *Wied. Ann.*, 26, 161 (1885); Ostwald: *J. prakt. Chem.*, 31, 433 (1885); Walker and Cormack: *J. Chem. Soc.*, 77, 11 and 12 (1901).

## CHAPTER VI.

### Dissociation of Electrolytes; Dissociation Constants.

**CLAUSIUS-WILLIAMSON HYPOTHESIS.**—It has long been known that during the electrolysis of a solution the dissolved substance was apparently broken up into two parts, one of which separated at the anode and the other at the cathode. For instance, when a current is passed through a solution of cupric chloride, copper separates at the cathode and chlorine at the anode. Faraday named these parts of the salt molecule ions, the one separating at the anode being called the anion and the one at the cathode the cation. Grotthuss accounted for this separation of the ions during electrolysis on the hypothesis that the current decomposed the molecules of the electrolyte into charged particles, and that those which were negatively charged—anions—were attracted to the positive pole or anode, while those which were positively charged—cations—were attracted to the negative pole or cathode.

Clausius, however, showed this hypothesis to be incorrect on account of the fact that Ohm's law holds for liquid as well as for metallic conductors—that is, that the current is always proportional to the electromotive force—and that, therefore, none of the energy of the current is used to decompose the molecules of the electrolyte. He stated, therefore, that ions must exist already formed, and ascribed as the cause of this condition the molecular motion of the substance in solution. This molecular motion consists of vibrations of the atoms of a molecule, as well as the rapid movement of the molecules themselves. As a result of this notion some of the molecules break up along the lines of least resistance, giving rise to ions. These ions are, of course, constantly recombining, but at any instant there is a certain average number existing in the free state These free ions with their charges are, therefore, moved toward the appropriate pole by the influence of the current. Williamson, working on etherification, had, shortly before this, also come to the conclusion that many substances in solution exist in a dissociated condition. It is, therefore, seen that the conception of the dissociation of salts in solution into ions has arisen from two entirely independent considerations.

The principal positive ions are hydrogen, the metals and the positive organic radicals, while the hydroxyl group and acid radicals, both inorganic and organic, are negative ions.

**FARADAY'S LAW.**—According to this law equal quantities of electricity are carried by equivalent quantities of electrolytes. It may also be stated as follows: Gram-equivalents of electrolytes or of ions always carry the same quantity of electricity, *viz.*, 96,580 coulombs.[1] Accordingly, it is clear that the quantity of an ion, separated at either pole by passing 1 coulomb of electricity through a solution, is $^1/_{96,580}$ gram-equivalent, or $0.000010354 \times W$ gram, where $W$ is the equivalent weight of the given ion based on $\frac{1}{2}O = 8$. Applying this to silver, for example, 1 coulomb of electricity will separate from a solution of silver nitrate $0.000010354 \times 107.93 = 0.0011175$ gram silver. This quantity is the electrochemical equivalent of the silver ion. In the case of copper (atomic weight 63.6), which is a bivalent ion, the electrochemical equivalent is $0.000010354 \times \frac{1}{2}63.6 = 0.0003293$ gram.

Since the ions carry charges of electricity proportional to their atomicity or quantivalence, the number and nature of the charges carried, as well as the number of ions formed from 1 molecule may be readily indicated in the following manner: Letting $+$ over the symbol of an ion represent a positive charge of electricity, and $-$ an equal negative charge, then NaCl dissociates into $\overset{+}{Na}$ and $\overset{-}{Cl}$, $BaCl_2$, into $\overset{++}{Ba}$ and $2\overset{-}{Cl}$, $CuSO_4$ into $\overset{++}{Cu}$ and $\overset{--}{SO_4}$, $AlCl_3$, into $\overset{+++}{Al}$ and $3\overset{-}{Cl}$, etc. Many substances dissociate in more than one way, as for instance, $H_2SO_4$ in very concentrated solutions dissociates into $\overset{+}{H}$ and $\overset{-}{HSO_4}$, but as the dilution increases the latter ion dissociates, so that in very dilute solutions the ions are $2\overset{+}{H}$ and $\overset{--}{SO_4}$. In electrochemical work it is frequently very convenient to represent the formulas of polyvalent electrolytes in terms of their equivalents, *viz.*, $\frac{1}{2}BaCl_2$, $\frac{1}{2}K_2CO_3$, $\frac{1}{2}CuSO_4$, $^1/_3AlCl_3$, etc.

**ARRHENIUS' THEORY; THE DEGREE OF DISSOCIATION.**—At any given concentration the magnitude of the conductivity of an

[1] Based on the standard silver voltameter according to Richards and Heimrod: *Ztschr. phys. Chem.*, 41, 302 (1902). A coulomb is the quantity of electricity which passes through a cross section of the conductor in one second when the current strength is one ampere.

electrolyte depends upon two factors, the relative number of molecules dissociated and the speed with which the ions move. The former of these, which was first given an exact definition by Arrhenius, will now be considered.

It had already been observed by Kohlrausch that as the dilution of a solution increases the equivalent conductivity also increases and tends to approach a maximum value. This maximum value is reached only at a very great, or, as it is termed, infinite dilution. Reasoning from these facts, Arrhenius stated that the equivalent conductivity of an electrolyte is a measure of its relative dissociation. The maximum conductivity at infinite dilution is due to all of the molecules being dissociated, that is, all of the molecules at this dilution are what he termed **active**. The equivalent conductivity is less at lower dilutions for the reason that many of the molecules are no longer active and that the number of active molecules decreases continually with the dilution. The number of active molecules is thus seen to be proportional to the equivalent conductivity, and, consequently, if $\Lambda_v$ is the equivalent conductivity at any dilution $v$, and $\Lambda_\infty$ the same at infinite dilution, the relative number of active or dissociated molecules at the dilution $v$ equals $\frac{\Lambda_v}{\Lambda_\infty}$.[1] This fraction, which is designated by $\alpha$, is called the degree of dissociation, and at any dilution is equal to the ratio of the equivalent conductivity at that dilution to the value of the equivalent conductivity of the same substance at infinite dilution. From the electrical conductivity, therefore, the degree of dissociation of an electrolyte in dilute aqueous solution may be readily determined.[2]

**OSTWALD'S DILUTION LAW.**—Starting from the law of mass action of Guldberg and Waage, Ostwald has derived an expression for the state of equilibrium in the dissociation of an electrolyte. When two substances unite to form a third, or a single sub-

[1] Arrhenius made use of the molecular conductivity, but since the facts are the same in either case, the equivalent conductivity is employed here in accordance with modern usage.

[2] This statement is restricted to dilute aqueous solutions because it apparently does not apply to concentrated aqueous solutions nor to many non-aqueous solutions. See, in this connection, Chapter 12.

stance breaks up into two others, and a state of equilibrium has been reached,

$$c_1 c_2 = kc.$$

In this expression $c$ is the concentration of the single substance, $c_1$ and $c_2$ are the concentrations of the two substances into which it decomposes, and $k$ is a constant. Applying this to the dissociation of a binary electrolyte, $c_1$ and $c_2$ are the concentrations of the two ions, respectively, which are, of course, equal, and $c$ is the concentration of the undissociated portion. In this case, therefore, the equation may be written $c_1^2 = kc$. Now since $c_1 = \frac{\alpha}{v}$ and $c = \frac{1-\alpha}{v}$, we have

$$\left(\frac{\alpha}{v}\right)^2 = k\frac{1-\alpha}{v}, \text{ or } \frac{\alpha^2}{(1-\alpha)v} = k^1.$$

If this equation holds $k$ must remain constant, while the dilution $v$ changes, it is, therefore, called the **dilution law**, and the constant $k$ is called the **dissociation constant.**

This dilution law of Ostwald holds excellently for weak electrolytes, that is, those which are only slightly dissociated in solutions of ordinary concentration. The constancy of $k$ is seen in the following examples with formic acid, acetic acid and ammonia. The conductivity in each case was measured at 25°.

| Formic Acid, $HCO_2H$. $\Lambda_\infty = 409$. | | | | Acetic Acid, $CH_3CO_2H$. $\Lambda_\infty = 395$. | | |
|---|---|---|---|---|---|---|
| 1. $v$. | 2. $\Lambda$. | 3. $\frac{100\alpha}{}$. | 4. $K$. | 2. $\Lambda$. | 3. $\frac{100\alpha}{}$. | 4. $K$. |
| 8 | 16.2 | 3.96 | 0.020 | 4.63 | 1.17 | 0.00174 |
| 16 | 22.6 | 5.53 | 0.020 | 6.50 | 1.65 | 0.00172 |
| 32 | 31.2 | 7.63 | 0.020 | 9.22 | 2.33 | 0.00174 |
| 64 | 43.2 | 10.56 | 0.019 | 12.89 | 3.26 | 0.00172 |
| 128 | 59.2 | 14.47 | 0.019 | 18.11 | 4.58 | 0.00172 |
| 256 | 80.6 | 19.71 | 0.019 | 25.39 | 6.43 | 0.00173 |
| 512 | 108.8 | 26.60 | 0.019 | 35.39 | 8.96 | 0.00172 |
| 1024 | 143.6 | 35.11 | 0.019 | 49.04 | 12.42 | 0.00172 |

[1] Kohlrausch uses $\phi$ in this equation instead of $v$ (see Chap. 1), in which case the constant has $\frac{1}{1000}$ the value of $k$ in this equation. To avoid many ciphers $K$ is frequently employed to indicate $1000k$.

AMMONIA, $NH_4OH$.

$\Lambda_\infty = 274$.

| 1. $v$. | 2. $\Lambda$. | 3. 100$\alpha$. | 4. $K$[1]. |
|---|---|---|---|
| 8 | 3.41 | 1.245 | 0.00193 |
| 16 | 4.74 | 1.73 | 0.00190 |
| 32 | 6.69 | 2.44 | 0.00191 |
| 64 | 9.49 | 3.46 | 0.00194 |
| 128 | 13.46 | 4.91 | 0.00198 |
| 256 | 19.06 | 6.96 | 0.00203 |

In column 1 is the dilution in liters, in column 2 the equivalent conductivity, in column 3 the percentage dissociation, that is, the degree of dissociation multiplied by 100, and in column 4 the constant $K$, which equals 100$k$.

**CONSEQUENCES OF THE DILUTION LAW.**—Comparing the results in the above table with the conductivity of strong electrolytes (KCl, etc., a few pages farther on), it is seen that with weak electrolytes the equivalent conductivity increases much more rapidly with the dilution than in the case of the strong electrolytes. It does not, however, increase in the same proportion as the dilution, but approximately as its square root. This relation necessarily follows from Ostwald's law, $\frac{\alpha^2}{(1-\alpha)v} = k$. For when the degree of dissociation is slight, $1-\alpha$ does not differ greatly from 1 and the equation becomes

$$\alpha^2 = kv, \text{ or } \alpha = \sqrt{kv} = k'\sqrt{v}.$$

Further relations can also be derived from this law. Since the migration number of hydrogen is a common factor of the conductivity of all acids, the value of $\Lambda_\infty$ does not vary greatly for different acids, and also the equivalent conductivities will be very nearly equal when the degrees of dissociation are equal. That is, if $\alpha_1$ is the degree of dissociation corresponding to $\Lambda_1$ for a certain concentration of one acid, and $\alpha_2$ and $\Lambda_2$ are similar values for such a concentration of another acid that $\alpha_1 = \alpha_2$, then $\Lambda_1$ is approximately equal to $\Lambda_2$. Now let

$$\frac{\alpha_1^2}{1-\alpha_1} = k_1 v_1 \text{ and } \frac{\alpha_2^2}{1-\alpha_2} = k_2 v_2,$$

[1] The recent work of Goldschmidt: *Physik. Zischr.*, 1, 287 (1900), has shown that $K$ is not constant for concentrated solutions of ammonia, which is in accord with our knowledge of the behavior of concentrated solutions.

be the dissociation equations of the two acids. Then at the concentrations where $\alpha_1 = \alpha_2$,

$$k_1 v_1 = k_2 v_2, \text{ or } \frac{v_1}{v_2} = \frac{k_2}{k_1} = \text{constant}; \text{ likewise } \frac{m_1}{m_2} = \text{constant}.$$

This means that the dilutions, or the concentrations, at which equivalent conductivities are equal are in a constant ratio, which is entirely independent of the absolute values of such conductivities. For instance, from the table on page 52 it is seen that $\Lambda$ for formic acid at $v = 8$ is equal to $\Lambda$ for acetic acid at $v = 100$ approximately, the same is true at $v = 16$ and 200, respectively, etc.

Furthermore, if we let $\alpha = 0.5$ in the original equation, some idea can be gained of the size of $k$ for different substances. Making this substitution, we have

$$\frac{0.25}{(1-0.5)v} = k,$$

from which

$$\frac{1}{2v} = k, \text{ or } \frac{1}{2} m = k.$$

This signifies, therefore, that the dissociation constant $k$ is equal to one-half the concentration, expressed in equivalents per liter, at which the electrolyte is one-half dissociated. Formic acid is 50 per cent. dissociated at a concentration approximately of $m = 0.0003$. The value of $k$ for this acid is seen to be not greatly different from one-half of this. The agreement is, however, much better with a very weak electrolyte as acetic acid. Since $k = 0.000017$ for this acid, it is one-half dissociated at a concentration of $m = 0.000034$, or at a dilution of about 29,400 liters.

**STRONG ELECTROLYTES AND THE LAW OF MASS ACTION.**—Ostwald's dilution law apparently does not hold for strong electrolytes, such as $HNO_3$ and KCl. Such substances are much too completely dissociated in concentrated solutions to be able to follow the law on dilution. The degree of dissociation of many such electrolytes, as determined according to the freezing-point method, differs considerably from that calculated from the conductivity. But even the values obtained by the former method do not

accord with the law of mass action, although they approximate it more nearly than those derived from the conductivity.

The theoretical grounds for this apparent failure of the dilution law with strong electrolytes has been the source of much investigation and discussion. The predominating opinion seems to be that it not necessary to discard entirely the theory of dissociation, but only to modify or supplement it. It has therefore been assumed that dissociation may be affected by the interaction of the ions, the non-dissociated molecules and the molecules of the solvent, this usually manifesting itself by a tendency of the simple ions to form more complex groups, either by combining with some of the solvent (hydration) or by uniting among themselves. That there is some truth in the hydrate theory has been shown recently by Jones and Getman[1], especially in the case of concentrated solutions. A. A. Noyes[2] has pointed out that the influence of the ions on each other and on the undissociated portion cannot be in accordance with the law of mass action, since both di-ionic salts follow the same empirical dilution formula, viz., that of Storch,

$$c(1-\gamma) = K(c\gamma)^n.$$

In this $c$ is the concentration of the salt, $\gamma$ is its degree of ionization, and $K$ and $n$ are constant, the value of $n$ for different salts varying only from 1.43 to 1.56.

Biltz,[3] by a comparison of the results obtained by means of applying osmotic and other physico-chemical methods to the investigation of solutions, arranges the univalent ions according to their tendency to deviate from the theoretical behavior of simple dissociation in the following order, this tendency decreasing from left to right:

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Cations..... | Li | Na | $NH_4$ | K | Rb | Cs | |
| Anions..... | I | F | Br | Cl | Cu | SCN | $NO_3$ |

He then assumes this to be the order in which the ions tend to form complex groups. Consequently, solutions of $RbNO_3$ and of $CsNO_3$ might be expected to follow quite closely the law of

[1] *Am. Chem. J.*, 31, 303 (1904).
[2] *Science*, 20, 577 (1904).

mass action, as exemplified in the Ostwald formula. Values of the dissociation $\alpha$, and of the Ostwald constant $k$, as calculated from the depression of the freezing-point and from the conductivity of solutions of these electrolytes, are given by Biltz as follows:

RUBIDIUM NITRATE.

| Freezing-point method. | | | Conductivity 25°. | | |
|---|---|---|---|---|---|
| $v$. | $\alpha$. | $k$. | $v$. | $\alpha$. | $k$. |
| 1.25 | 0.429 | 0.27 | 4 | 0.764 | 0.62 |
| 1.695 | 0.504 | 0.31 | 8 | 0.815 | 0.44 |
| 2.625 | 0.619 | 0.39 | 16 | 0.875 | 0.38 |
| 5.19 | 0.731 | 0.39 | 32 | 0.908 | 0.28 |
| 8.65 | 0.792 | 0.35 | 64 | 0.927 | 0.18 |
| 25.5 | 0.941 | 0.47 | 128 | 0.947 | 0.13 |

CAESIUM NITRATE.

| | | | | | |
|---|---|---|---|---|---|
| 2.33 | 0.578 | 0.34 | .. | .... | ... |
| 3.385 | 0.641 | 0.34 | 4 | 0.761 | 0.61 |
| 4.81 | 0.704 | 0.35 | 8 | 0.822 | 0.47 |
| 7.09 | 0.750 | 0.32 | 16 | 0.872 | 0.37 |
| 10.2 | 0.810 | 0.34 | 32 | 0.913 | 0.30 |
| 51.6 | 0.95 | 0.35 | 64 | 0.941 | 0.23 |
| 130.7 | 0.98 | 0.33 | 128 | 0.948 | 0.14 |

The constancy of $k$ for rubidium nitrate when derived from the cryoscopic measurements is only fair, while for caesium nitrate it is excellent, so we have here the first example of a strong electrolyte which follows Ostwald's dilution law.[1]

**LIMITATION OF THE EQUATION, $\alpha = \frac{\Lambda_v}{\Lambda_\infty}$.** The dissociation of the above salts, when calculated from the conductivity, does not, however, give a constant value for $k$. It has already been mentioned that the freezing-point method and the conductivity method yield different values for the degree of dissociation in the case of most strong electrolytes; consequently, the accuracy of the equation, $\alpha = \frac{\Lambda_v}{\Lambda_\infty}$, for strong electrolytes has frequently been questioned, notably by Jahn,[2] who has estimated that in the case

[1] Picric acid, a strong electrolyte, whose dissociation as calculated by the freezing-point or conductivity method does not follow the law of mass action, has just been found by Rothmund and Drucker to do so when the dissociation is derived from its partition between the solvents benzene and water. *Ztschr. phys. Chem.*, 46, 827 (1903).

[2] *Ztschr. phys. Chem.*, 33, 545 (1900).

of electrolytes like NaCl it gives results about 10 per cent. too high.[1] From the results of Biltz, just given, the only inference is that the Arrhenius equation is, indeed, unreliable when applied to strong electrolytes, and that the deviation from the true value is not constant, but is a function of the electrolyte itself. The true value of the degree of dissociation is also not given by cryoscopic measurements, except in the case of certain electrolytes which approximate the limiting conditions pointed out by Biltz. This latter method is, however, undoubtedly less influenced by the secondary reactions, which take place in the solution of strong electrolytes, than the conductivity method.

Steele[2] has recently derived a relation to express the degree of dissociation of electrolytes having complex anions,[3] which shows that in some cases the equation, $\alpha = \frac{\Lambda_v}{\Lambda_\infty}$, cannot be expected to yield the true value of the dissociation as long as the dilution is such that the complex ion is present.

Defining the degree of dissociation as the ratio of the concentration of the ions of one kind—in this case cations—to the total concentration of the electrolyte, we have $x = \frac{c}{\eta}$, in which $x$ is the degree of dissociation thus defined, $c$ the concentration of the cation and $\eta$ the total concentration of the electrolyte. The specific conductivity of this solution then is

$$\kappa = \varepsilon[c(l_c + l_a) - c'(l_a - l_{a'})].$$

In this $c$ has the same signification as above, $c'$ is the concentration of the complex anion, $l_c$, $l_a$, and $l_{a'}$ are migration numbers[4] of the cation, the simple anion and the complex anion respectively, and $\varepsilon$ is the quantity of electricity carried by 1 gram-equivalent.

Now letting $\beta = \frac{c'}{c}$, we have

[1] See in this connection Noyes: *Science*, **20**, 579 (1904).

[2] *Zischr. phys. Chem.*, **40**, 730 (1902).

[3] Such as $Na_2SO_4$, which undoubtedly dissociates partly into $\overset{+}{Na}$ and $\overset{-}{NaSO_4}$, and partly into $2\overset{+}{Na}$ and $\overset{=}{SO_4}$.

[4] For an explanation of the migration numbers see the next chapter.

$$\kappa = \varepsilon c[(l_c + l_a) - \beta(l_a - l_{a'})].$$

For any other concentration

$$\kappa_1 = \varepsilon c_1[(l_c + l_a) - \beta_1(l_a - l_{a'})].$$

Now since $\Lambda = \frac{\kappa}{\eta}$,

$$\frac{\Lambda}{\Lambda_1} = \frac{\frac{c}{\eta}[(l_c + l_a) - \beta(l_a - l_{a'})]}{\frac{c_1}{\eta_1}[(l_c + l_a) - \beta_1(l_a - l_{a'})]}.$$

At infinite dilution $c = \eta$ and $\beta = 0$, and therefore

$$\frac{\Lambda}{\Lambda_\infty} = \frac{x[(l_c + l_a) - \beta(l_a - l_{a'})]}{l_c + l_a},$$

from which

$$x = \frac{\Lambda}{\Lambda_\infty} + \beta x \frac{l_a - l_{a'}}{l_c + l_a}.$$

Therefore only when $l_a = l_{a'}$ or $\beta = 0$, does $\frac{\Lambda}{\Lambda_\infty}$ represent the true degree of dissociation. Even in the case of strong binary electrolytes $\frac{\Lambda}{\Lambda_\infty}$ may not always represent the true degree of dissociation; for, as we have already seen, complex ions of some sort doubtless exist in such solutions.

**DILUTION FORMULAS FOR STRONG ELECTROLYTES.**—Ostwald's dilution law does not hold for solutions of strong electrolytes, as the strong acids and bases and most neutral salts. Such substances are much too completely dissociated in concentrated solutions to be able to follow the law on dilution. The reason that such electrolytes do not obey the law has not as yet been satisfactorily explained. One possible explanation is that the ions of strong electrolytes may increase the dissociating power of water. The addition of a non-electrolyte to water, we know, decreases the dissociating power of water, hence it is argued the presence of strong electrolytes may increase it. Arrhenius[1] appears to have found grounds for this view in investigating the dissociation of weak acids in the presence of salts. The disso-

[1] *Ztschr. phys. Chem.*, 31, 211 (1899).

ciation constants of salts, calculated according to the Ostwald formula, increase as the concentration of the solution increases. The dissociation constants of the weak acids in Arrhenius' experiment increased also as the concentration increased, although not so much as the constants of strong electrolytes.

Others have sought to explain this apparent inapplicability of the law of mass action in this case on the ground that Arrhenius' equation for the degree of dissociation, $\alpha = \frac{\Lambda_v}{\Lambda_\infty}$, does not hold for solutions of strong electrolytes. It is true that the degree of dissociation, as found by the freezing-point method, does, in some cases vary considerably from that found by the above equation. However, the agreement is, in many cases, so perfect that the burden of proof must be thrown on the opponents of the Arrhenius equation.[1]

Several formulas of an empirical nature connecting the degree of dissociation of strong electrolytes with the dilution have been proposed. Of these Rudolphi's[2] differs from Ostwald's in substituting for the dilution $v$ its square root, so that it has the form,

$$\frac{\alpha^2}{(1-\alpha)\sqrt{v}} = \text{constant}.$$

The value of this constant for potassium and sodium chlorides is shown in the fourth column of the table below. The conductivity determinations were made by Kohlrausch and Maltby[3] at 18°, and are the most recent figures for these electrolytes. The values of the expression $\frac{\alpha^2}{(1-\alpha)\sqrt{v}}$ are seen to be fairly constant, but show a gradual falling off with increasing dilution.

Another empirical dilution formula is that of van't Hoff.[4] We have seen that the Ostwald dilution formula is derived from the expression,

[1] See besides the discussion on pp. 55-58 the following: Euler: *Ztschr. phys. Chem.*, 29, 603 (1899); Biltz: *Ibid.*, 40, 185 (1902); Goebel: *Ibid.*, 42, 59 (1902); Jahn: several articles, see especially *Ibid.*, 41, 257 (1902); Sackur: *Ztschr. Elektrochem.*, 7, 784 (1901); Liebenow; *Ibid.*, 8, 933 (1902).

[2] *Ztschr. phys. Chem.*, 17, 385 (1895).

[3] *Sitzungsber. Kgl. pr. Akad. Wiss.*, Berlin, 1899, p. 665.

[4] *Ztschr. phys. Chem.*, 18, 300 (1895).

$$\frac{\left(\frac{\alpha}{v}\right)^2}{\frac{1-\alpha}{v}} = \text{constant},$$

which signifies that the ratio of the square of the concentration of the dissociation portion of an electrolyte to the concentration of the undissociated portion is constant. Van't Hoff makes the ratio of the cube of the concentration of the dissociated portion to the square of the concentration of the undissociated portion to constant. Accordingly, he obtains the relation,

$$\frac{\left(\frac{\alpha}{v}\right)^2}{\left(\frac{1-\alpha}{v}\right)^3} = \text{constant},$$

or simplified

$$\frac{\alpha^2}{(1-\alpha)\sqrt{v}} = \text{constant},$$

The value of this expression is given in the fifth column below. The degree of constancy is nearly as good as when Rudolphi's formula is used. But, of course, the theoretical basis is as much unexplained in one case as in the other.

POTASSIUM CHLORIDE, KCl.

$\Lambda_\infty = 130.1.$

| $v$. | $\Lambda$. | 100$\alpha$. | $\frac{\alpha^2}{(1-\alpha)\sqrt{v}}$. | $\frac{\alpha^2}{(1-\alpha)\sqrt{v}}$. |
|---|---|---|---|---|
| 10 | 112.00 | 86.08 | 1.68 | 1.81 |
| 20 | 115.94 | 89.11 | 1.63 | 1.73 |
| 50 | 120.00 | 92.23 | 1.55 | 1.61 |
| 100 | 122.42 | 94.09 | 1.50 | 1.54 |
| 200 | 124.40 | 95.61 | 1.47 | 1.51 |
| 500 | 126.29 | 97.06 | 1.43 | 1.45 |
| 1000 | 127.33 | 97.86 | 1.42 | 1.43 |
| 2000 | 128.09 | 98.45 | 1.40 | 1.41 |
| 5000 | 128.76 | 98.96 | 1.34 | 1.34 |

SODIUM CHLORIDE, NaCl.

$\Lambda_\infty = 109.0.$

| | | | | |
|---|---|---|---|---|
| 10 | 92.01 | 84.42 | 1.45 | 1.57 |
| 20 | 95.86 | 87.95 | 1.44 | 1.53 |
| 50 | 99.66 | 91.44 | 1.38 | 1.44 |
| 100 | 101.95 | 93.54 | 1.36 | 1.40 |
| 200 | 103.79 | 95.23 | 1.34 | 1.38 |
| 500 | 105.55 | 96.62 | 1.24 | 1.26 |
| 1000 | 106.48 | 97.70 | 1.31 | 1.33 |
| 2000 | 107.18 | 98.34 | 1.30 | 1.31 |
| 5000 | 107.80 | 98.91 | 1.27 | 1.28 |

Still other dilution formulas have been proposed besides those already mentioned, but none of them are on any firmer theoretical foundation. Many of them have been devised in order to calculate the conductivity of an electrolyte at a given dilution. They follow the actual determinations quite closely in certain cases, but are cumbersome to use owing to the employment of one or more arbitrary constants for each electrolyte.[1]

**LIMITATION TO BINARY ELECTROLYTES.**—The dilution formulas which have just been discussed, apply only to binary electrolytes. In the case of electrolytes which dissociate into three or more ions the conditions are much more complicated, and no such simple relations as the above are to be expected. Most of the dibasic organic acids, however, follow Ostwald's dilution formula owing to the fact that an acid of the strength of succinic, for example, is dissociated into only two ions. In the case of this acid, $H_2C_4H_4O_4$, the two ions are H and $HC_4H_4O_4$, only one of the carboxyl Hs being dissociated. The constancy of $k$ for succinic acid, according to Ostwald's formula, is shown in the following table. The measurements were made at 25°.

SUCCINIC ACID, $H_2C_4H_4O_4$.

$\Lambda_\infty = 387$.

| $v$. | $M$[2]. | 1000 $k$. | $K$. |
|---|---|---|---|
| 16 | 12.2 | 3.15 | 0.0064 |
| 32 | 17.2 | 4.44 | 0.0065 |
| 64 | 24.1 | 6.23 | 0.0065 |
| 128 | 33.5 | 8.66 | 0.0064 |
| 256 | 46.7 | 12.07 | 0.0065 |
| 512 | 63.8 | 16.49 | 0.0064 |
| 1024 | 88.2 | 22.80 | 0.0066 |

**MOVEMENT OF THE IONS.**—It has been shown that one of the factors on which the conductivity of a solution depends is the degree of dissociation of the substance dissolved. The second factor influencing conductivity is the **relative rate** at which the ions move. This is directly dependent on the friction which the ions experience in rubbing against one another and against the molecules of the solvent as they move through the solution. The

[1] See Kohlrausch: *Ztschr. phys. Chem.*, 18, 662 (1895); Storch: *Ibid.*, 19, 13 (1896); Barmwater: *Ibid.*, 28, 130 (1899); Bancroft: *Ibid.*, 31, 188 (1899).

[2] $M$ is the molecular conductivity.

friction varies with the nature of the ion and the concentration of the solution.

The hydrogen ion experiences the least friction and consequently has the greatest speed, or greatest rate of migration, as it is sometimes termed, of any of the ions. The hydroxyl (OH) ion moves next fastest, having a velocity a little more than half that of the hydrogen ion. The acid radicals and the metallic ions have rates of migration varying from one-fifth to one-tenth that of the hydrogen ion, while complex organic ions move the most slowly.

The effect of increasing the concentration of a solution is, in general, to increase the friction and retard the movement of the ions. In dilute solutions, however, if the concentration is kept below a certain limit—about tenth-normal—changes of concentration have little or no effect in this respect. As the concentration increases above this limit the friction of the ions increases, and in very concentrated solutions the velocity of the ions is noticeably affected thereby. In such concentrated solutions it has thus far been found impossible to separate the effect of the electrolytic friction of the ions from that of the dissociation of the substance, so that for this reason, as well as for others, it has not been found practicable to base the conductivity of concentrated solutions on a definite theoretical basis.

As the concentration is increased the specific conductivity of electrolytes does not increase in the same ratio, but usually very much slower. In fact, there are many cases where the conductivity reaches a maximum value and then decreases as the concentration continues to increase. Such is the conduct of those electrolytes that mix with water in all proportions; for, since mixing increases the degree of dissociation over that either of water or of the pure substance, there must be a concentration of maximum specific conductivity between the two.

Sulphuric acid affords a good illustration of this. The maximum conductivity is found at a concentration of 30 per cent. Below this the conductivity decreases with the concentration. Above this point, however, the conductivity gradually decreases with increase of concentration up to 84.5 per cent. (corresponding to the hydrate $H_2SO_4 + H_2O$). As the concentration increases above 84.5 per cent. the conductivity slowly increases until the

concentration reaches about 92 per cent., above which the conductivity rapidly decreases to the conductivity of pure $H_2SO_4$. On the addition of $SO_3$ to the pure acid there is first an increase of conductivity, then later the conductivity falls off very rapidly to zero, since pure $SO_3$ is a non-conductor. This shows very strikingly the effect of mixing, for with increasing concentration we have passed through three maxima, *viz.*, one between water and $H_2SO_4 + H_2O$, another between $H_2SO_4 + H_2O$ and $H_2SO_4$, and the third between $H_2SO_4$ and $SO_3$.

## CHAPTER VII.

### The Migration of the Ions.

**THE LAW OF KOHLRAUSCH.**—Long before the theory of dissociation had been enunciated, Kohlrausch,[1] in comparing the equivalent conductivities of different electrolytes in very dilute solution, noticed that the values of such conductivities can be resolved into two factors, one depending on the nature of the anion alone and the other on the nature of the cation alone. This relation at infinite dilution may be expressed as follows:

$$\Lambda_\infty = l_a + l_c,^2$$

in which $l_a$ is the factor depending on the anion and $l_c$ the one depending on the cation. These quantities, which are expressed in the same units as the equivalent conductivity, are proportional to the velocities of the ions. In order to distinguish them, however, from the absolute velocities of the ions, they will be called **migration numbers.** The above equation signifies that at a dilution at which an electrolyte is completely dissociated into its ions, its equivalent conductivity is simply the sum of the migration numbers of the anion and of the cation. Since $\alpha = \frac{\Lambda_v}{\Lambda_\infty}$, it follows that

$$\Lambda_v = \alpha(l_a + l_c).$$

This expresses the relation between the migration numbers of the ions and the equivalent conductivity at any concentration $v$.

**CHANGE OF CONCENTRATION ABOUT THE ELECTRODES.**—Hittorf was the first to establish the fact that the ions travel at different speeds. Previous to the time of Hittorf it was known that the concentration of an electrolyte frequently underwent a change about one of the electrodes different from that about the other. Hittorf[3] ascribed this change of concentration to the different speeds at which the ions travel. He made the first measurements which lay any claim to exactness to determine these changes

[1] *Göttinger Nachrichten*, 1876, p. 213; *Wied. Ann.*, 6, 167 (1879).

[2] According to the old system of units instead of $l_a$ and $l_c$, $u$ and $v$ were used to designate these factors, and the equation ran $\lambda_\infty = u + v$, or $\mu_\infty = u + v$.

[3] *Pogg. Ann.*, 89, 177 (1853), and many other articles in later volumes of this journal.

of concentration, and from these he calculated the relative velocities of the ions.

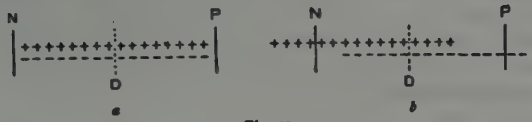



Fig. 15.

It can readily be shown by means of diagrams, Fig. 15, how a difference in the velocities of the ions is able to cause a change of concentration about the electrodes. Let the cations be represented by + and the anions by — and suppose the ions to be arranged in the solution in rows, as in Fig. 15*a*, there being an equal number of each kind of ions on each side of the porous diaphragm *D*. Since 8 molecules are present in each compartment the original concentration about each electrode may be represented by 8.

Now let us suppose a current to be passed and the cations to move twice as fast as the anions. After a certain interval the conditions may be represented by Fig. 15*b*. Each ion, which has no partner, is supposed to be set free and discharged at the electrodes. Six positive and six negative ions have, therefore, been liberated. The concentration in the cathodic compartment has decreased from 8 to 6, while in the anodic compartment it has decreased from 8 to 4, a loss of 2 and 4 respectively. This means that the loss in concentration around the cathode is to the loss in concentration around the anode as the velocity of the anion is to the velocity of the cation; that is, the losses in concentration about the electrodes are inversely proportional to the speeds of the correspondingly named ions. If, therefore, the change in concentration around the electrodes is accurately determined after a certain interval of electrolytic action, the relative velocities of the ions, or as they are termed **transport numbers**, can be at once ascertained.

**HITTORF'S METHOD FOR DETERMINING TRANSPORT NUMBERS.**—As has already been stated, the method just outlined was first employed by Hittorf, and it is, therefore, usually known by

his name. It is sometimes known as the indirect method, for the reason that the velocities of the ions are not directly measured, but are deduced from the change in concentration of the solution during electrolysis. The determination of the transport numbers of the ions of silver nitrate, by Loeb and Nernst,[1] affords an excellent example of this method on account of the simplicity of the apparatus employed.

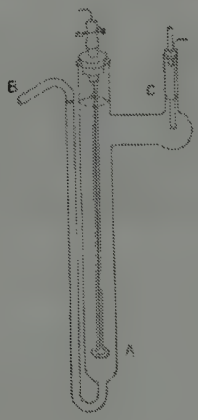



Fig. 16.

The kind of electrolytic vessel used by them is shown in Fig. 16. Convection currents must, of course, be avoided, and to insure this, diaphrams are used in many forms of apparatus. Here, however, no diaphragm is required, because the form of the vessel is designed to prevent diffusion, the heavier portion of the solution, at the end of the experiment, being in the lower portion of the apparatus. The cathode *C* is a piece of silver foil cylindrically rolled, and the anode *A* consists of a flat spiral of silver wire. This wire, where it passes through the solution, is covered with a glass capillary tube to prevent contact with the liquid. The opening at *B* is so arranged that the apparatus can be filled or emptied while in a constant temperature bath. The vessel is filled with a

[1] *Ztschr. phys. Chem.*, 2, 948 (1888).

known quantity of silver nitrate solution of known strength, and a feeble current is passed for some hours, the quantity of electricity being measured by a voltameter. At the termination of the experiment approximately one-third of the solution is removed at $B$ (anode portion) and the amount of silver determined in it analytically; a second third of the solution (middle portion) is then removed and analyzed; finally, the last third remaining in the vessel (cathode portion) is analyzed. If the experiment was successful the concentration of the middle portion should remain unchanged, showing that there were no disturbing convection currents.

In an experiment of this kind the total amount of silver nitrate in the solution has not changed, because for every Ag ion which separated out at the cathode one went into solution at the anode. There was no separation of $NO_3$ ions from the solution, as they simply dissolved silver from the anode. The concentration was continually increasing about this pole, due to the migration of $NO_3$ ions in this direction.

In an actual experiment 32.2 mg. silver were deposited in the voltameter, while the concentration of silver around the anode increased 16.8 mg. and around the cathode decreased by this amount. If no Ag ions had migrated from the anode the concentration would have increased around this pole by 32.2 mg. silver, so the fall in concentration, due to the migration of Ag ions, was actually $32.2 - 16.8 = 15.4$ mg. silver. Therefore, since the relative speeds of the ions are proportional to the fall of concentration around the oppositely named electrode we have

$$\frac{\text{Speed of anion } (NO_3)}{\text{Speed of cation (Ag)}} = \frac{\text{Fall around cathode}}{\text{Fall around anode}} = \frac{16.8}{15.4} = 1.091 = r.$$

This quantity $r$ is the ratio of the rate of migration of the anion to that of the cation.

The transport number of the anion $n$ is the ratio of its share in the transport of electricity to the total transport of electricity. This is equal to the ratio of the speed of the anion to the sum of the speeds of both ions, that is, since the migration numbers are proportional to the speeds of the ions,

$$n = \frac{l_a}{l_a + l_c}.$$

$$\frac{l_c}{l_a + l_c} = 1 - n.$$

From the relation

$$r = \frac{l_a}{l_c} = \frac{n}{1-n},$$

we also have

$$n = \frac{r}{1 + r}.$$

If we substitute for $r$ in this equation its value as found above for silver nitrate, we obtain

$$n = \frac{1.091}{1 + 1.091} = 0.522.$$

0.522 is, therefore, the share in the transport of electricity taken by the $NO_3$ ion in a solution of silver nitrate. The share taken by the Ag ion is $1 - 0.522 = 0.478$. We can also obtain $n$ directly from the losses in concentration around the electrodes, since these are proportional to the speeds of the ions and to the migration numbers. Accordingly, we have from the above experiment

$$n = \frac{l_a}{l_a + l_c} = \frac{16.8}{16.8 + 15.4} = 0.522.$$

Hittorf's method of determining transport numbers has been used by a great number of investigators[1] and has yielded very satisfactory results. It is the most trustworthy method in use, because its sources of error and the conditions necessary to secure a high degree of accuracy seem to be quite clearly understood.

**THE DIRECT METHOD OF DETERMINING THE VELOCITY OF THE IONS.**—The method of Hittorf, as has already been shown, is an indirect method for the reason that the velocities of the ions are derived from changes of concentration around the electrodes. The first successful attempt to measure directly the velocity of

[1] For the most recent work with this method see the following: Hopfgartner: *Ztschr. phys. Chem*., 28, 113 (1898); Bein: *Ibid*., 27, 1 (1898); Starck: *Ibid*., 29, 385 (1899); Jahn and Students: *Ibid*., 37, 673 (1901); Mather: *Am. Chem. J*., 26, 473 (1901); Noyes: *J. Am. Chem. Soc*., 23, 37 (1901); Noyes and Sammet: *Ibid*., 24, 944 (1902); Steele and Denison: *J. Chem. Soc*., 81, 456 (1902). For certain sources of error, with semipermeable membranes, and for corrections to former results, see Hittorf: *Ztschr. phys. Chem*., 39, 613 (1902); and 43, 239 (1903).

the one due to Lodge.[1] Methods, depending on the same principle, have since been employed by Whetham,[2] Masson,[3] and Steele,[4] each one of whom added substantial improvements to the method as practised by his predecessors. This method is of late much applied, due to Hittorf, both on account of the limitations in the choice of indicator solutions (see below) and because of the fact that it cannot be applied with accuracy to very dilute solutions.

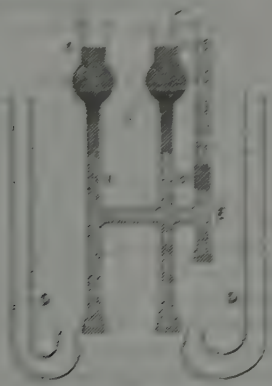


Fig. 17

The method, as used by Steele, consists essentially in using the movement of the boundary between a pair of solutions subject to electrolysis. The solution into which the boundary moves contains the electrolyte, the speed of whose ion is to be determined, while the other, which is colourless, contains an electrolyte, the so-called indicator. The electrolyte under investigation is provided at each end by such an indicator solution. For instance, when determining the speeds of the ions of potassium chloride, the solution used at the anode was sodium acetate and at the cathode barium chloride.

[1] Brit. Ass. Reports, 1886, p. 389.
[2] Phil. Trans. 1893, A. 337; 1897, A. 321; also Zeitsch. phys. Chem., 11, 220, (1893).
[3] Zeitsch. phys. Chem. 29, 321, (1899).
[4] Independently the same principle is the following journals: Phil. Trans., 1901, A. 105; Chem. Soc. 79 and 1901. Zeitsch. phys. Chem. 36, (1901).

The form of apparatus best adapted to the investigation of the simplest type of salts is shown in Fig. 17. The tubes *A* and *B* contain the electrolyte under investigation. To *B* is attached the tube *E* so that the solution will be under atmospheric pressure throughout the experiment. Each tube can be connected with the larger tubes *C C* at the top, or *D D* at the bottom, which contain the gelatinized indicator solutions. When both indicator solutions are lighter than the solution in *A B*, they are placed in the upper vessels, *C C*; when they are both heavier in the lower ones, *D D*; when one is lighter and one is heavier, the lighter is placed in *C* and the heavier in *D*.

When a current is passed, the boundaries move into the tubes *A B* with a speed, which, under certain conditions, depends only on the nature of the ion ahead and on the electromotive force. The motion of the boundary can be easily followed by the difference in refraction of the two layers, a small gas flame being placed behind the apparatus to illuminate the tube.

It is necessary for the success of an experiment that the speed of the indicator ion be less than that of the ion whose speed is being measured, that the resistance of the indicator solution be only a trifle greater than that of the solution it follows, and that the electromotive force be kept within certain limits determined by trial. The selection of a suitable indicator is, in the case of many solutions, a matter of considerable difficulty. No indicators that split up hydrolytically can be used on account of the great speed of H and OH ions.

The distances traveled by the two boundaries and hence by the two ions are read off at certain intervals by means of a cathetometer. From these readings and the current measurements made at the same times the ratio $\frac{l_a}{l_c}$ or $r$ is easily obtained, from which $n$, the transport number of the anion, can be readily calculated.

The transport numbers obtained by Masson and by Steele differ in a good many instances from those determined according to the method of Hittorf. Abegg and Gaus[1] have, consequently, subjected Steele's method to a critical investigation in order to discover possible sources of error.

They point out certain additional conditions, which must be fulfilled in order to avoid inaccuracy, and they furthermore have shown experimentally that the deviation from Hittorf's results is not due to variable current strength, but to the fact that the electrolyzed solution is cataphoretically transported even through the relatively dense gelatinous layers. Correcting for this cataphoresis which they measured in the case of half-normal potassium chloride, Steele's value of 0.490 for the transport number of the anion becomes 0.508, in good agreement with the values obtained by Hittorf's method with potassium chloride solutions of the same concentration.

Denison[1] has continued the investigation of Steele's method, and the results of his work may be summed up as follows:

After making the proper correction for cataphoresis the transport numbers of all the alkali metals, except lithium, agree with those obtained by the method of Hittorf.

In cases where complex ions are formed or hydrolysis takes place the numbers do not agree with those of Hittorf.

It is probable that gelatine is able to combine with some salts, giving rise to complex ions.

The gelatine solutions should be kept in the liquid condition; for in solid gelatine solutions the speed of the cation, relative to that of the anion, seems to be lessened, as is apparently also the case in concentrated aqueous solutions.

**VALUES OF TRANSPORT NUMBERS OF SOME UNIVALENT ELECTROLYTES.**—Transport numbers vary somewhat with the temperature and also with the concentration of the solution. Unfortunately no standard temperatures or concentrations have been employed in determining these numbers, as has been the case in measuring conductivity. The transport numbers of most univalent—or, as they are frequently called because they dissociate into only two ions, binary—electrolytes vary but little with the temperature. The values found by Bein for the transport number of the anion of potassium, sodium and lithium chlorides, at different temperatures, are shown below.

| | 10°. | 20°. | 51°. | 76°. | 97°. |
|---|---|---|---|---|---|
| Potassium chloride .... | 0.503 | .... | .... | 0.513 | .... |
| Sodium chloride ..... | 0.615 | .... | 0.583 | .... | 0.547 |
| Lithium chloride ..... | .... | 0.624 | .... | .... | 0.621 |

[1] Zeitsch. Phys. Chem. 44, 207 (1903).

For concentrations less than fifth-normal Bein could detect no variation of the transport numbers of potassium and sodium chlorides with the concentration. For lithium chloride, however, at 20° the transport number varies from 0.672 at a concentration of fifth-normal to 0.624 at hundredth-normal.[1] In general, the transport numbers of most binary electrolytes vary but little with the concentration, provided that the concentration does not exceed tenth-normal. Jahn and Bogdan's results with dilute solutions of sodium and potassium chlorides are shown in the accompanying table.

| v. | NaCl. | KCl. |
|---|---|---|
| 30 | 0.605 | 0.505 |
| 60 | 0.603 | 0.502 |
| 90 | 0.604 | 0.502 |
| 120 | 0.605 | 0.503 |

For electrolytes whose transport numbers show no variation below a certain concentration, the correct values of the transport numbers at infinite dilution are considered to be equal to this constant number. Such constant values of the transport numbers of some univalent electrolytes are given in the table below. They are taken from the sources already mentioned and are given, as nearly as possible, in the order of their trustworthiness.

TRANSPORT NUMBERS OF THE ANION AT MEAN TEMPERATURE (ABOUT 20°) IN DILUTE SOLUTION.

| | | |
|---|---|---|
| Potassium chloride | 0.504 | at 18°. For other temperatures $n_t = n_{18} + 0.0009(t-18)$. |
| Hydrochloric acid | 0.166 | |
| Silver nitrate | 0.529[2] | |
| Potassium nitrate | 0.495 | |
| Sodium chloride | 0.604 | |
| Ammonium chloride | 0.507 | |
| Lithium chloride | 0.670 | |
| Potassium hydroxide | 0.73 | |

**MIGRATION NUMBERS OF UNIVALENT IONS.**—The migration numbers of the ions, $l_a$ and $l_c$, can be calculated from the equiv-

[1] Interesting in this connection is the relative tendency of the simple ions to form more complex ones, as shown by Biltz. (See page 55.)

[2] The commonly accepted value 0.528 has been raised somewhat on account of the publication of Mather's results: *Am. Chem. J.*, 26, 485 (1901). The average of Jahn and Berliner's results give this same value, *viz.*, 0.529; *Zischr. phys. Chem.*, 37, 695 (1901).

alent conductivity by means of the transport numbers according to relations already given, *viz.*,

$$\Lambda_\infty = l_a + l_c,\ n = \frac{l_a}{l_a + l_c},\ \text{and}\ 1-n = \frac{l_c}{l_a + l_c}.$$

From these we obtain

$$l_a = n\Lambda_\infty,\ \text{and}\ l_c = (1-n)\Lambda_\infty.$$

The migration numbers of the more important univalent ions are given in the table below. They have been calculated from the values of $\Lambda_\infty$ given in the next chapter, and are based on the first four transport numbers in the above table. The relative weight given to each transport number is in accordance with the order in which they are given in the table. Values not given directly from these four transport numbers were computed by difference.

MIGRATION NUMBERS OF UNIVALENT IONS.

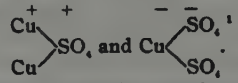
| Anions. | | | Cations. | | |
|---|---|---|---|---|---|
| | 18°. | 25°. | | 18°. | 25°. |
| Cl..... | 65.6 | 75.7 | K..... | 64.5 | 74.4 |
| Br ..... | 67.8 | 78.2 | Na..... | 43.4 | 51.1 |
| I..... | 66.6 | 76.8 | $NH_4$ ... | 64.2 | 74.4 |
| F ..... | 46.8 | 54.6 | Li ..... | 33.3 | 39.3 |
| $NO_3$.... | 62.0 | 71.2 | Rb .... | 67.4 | 77.3 |
| $ClO_3$.... | 55.2 | 63.7 | Cs..... | 68.0 | 77.9 |
| $IO_3$..... | 34.0 | ... | Ag .... | 54.0 | 62.9 |
| SCN.... | 56.8 | ... | Tl ..... | 65.9 | ... |
| $C_2H_3O_2$ . | 35.0 | 43.0 | H[1]..... | 318.0 | 352.0 |
| OH..... | 176.5 | 199.5 | | | |

**TRANSPORT NUMBERS OF BIVALENT ELECTROLYTES.**—As has already been intimated, the dissociation of bivalent electrolytes, as $CaCl_2$, $K_2SO_4$ and $CuSO_4$, is of a more complex nature than that of univalent ones. For instance, we believe that in solutions not too dilute barium chloride may yield besides the ions Ba and Cl, the more complex one $BaCl$ or even $BaCl_3$, or $BaCl_4$.[2] However, in the case of the salts of the strong acids the complex ions on dilution are probably finally all decomposed into the simpler ones, so that beyond a certain concentration only simple ions exist. Similarly, in dilute solutions of $K_2SO_4$, besides the simple

[1] Noyes and Sammet (*J. Am. Chem. Soc.*, 24, 944 (1902)) from experiments with hydrochloric acid found this quantity to be 330 at 18°, and 365 at 25°. However, more recent work in Noyes' laboratory has convinced him that these are too high, consequently the value adopted by Kohlrausch is given in the table.

[2] See Noyes: *J. Am. Chem. Soc.*, 23, 54 (1901).

ions K and $SO_4$, there exists also the ion $KSO_4$, and in solution of $CuSO_4$ very likely the ions



Since the nature of the ions is thus changing on dilution, we should expect to find the transport numbers varying at different concentrations. This is in fact the case, and is due probably both to the change in the ratio of the number of anions to the number of cations and to the fact that these different ionic aggregations undoubtedly possess different speeds. If, however, the transport number of a bivalent electrolyte becomes constant on diluting, we may infer that at this dilution the only ions present in measurable quantity are the simple ones and that this constant value is also the correct transport number at infinite dilution.

It is difficult in solutions whose concentration is less than 0.01 normal to determine accurately transport numbers by the Hittorf method and absolutely impossible by the direct method. By means of the Hittorf method it has been found, however, that some bivalent electrolytes yield transport numbers apparently constant near this concentration, or at least are approaching a constant value which can be extrapolated without great error. Some transport numbers, determinations of which have been carried out for dilute solutions, are given below. The values are all based on half molecules, and $v$ is, therefore, the number of liters in which a gram-equivalent is dissolved, and $m$ is the corresponding equivalent concentration. The numbers represent transport numbers of the anion at temperatures in the vicinity of 20°.

Starck's transport numbers of sulphuric acid show a continuous decrease with the concentration to sixteenth-normal, while Hittorf's results show an apparent increase as the concentration decreases from normal. For concentrations greater than normal (not given above) Starck is in accord with others in finding that the value of the transport number increases with the concentration. Bein's value at the concentration twentieth-normal is nearly the mean of the values found by Hittorf and by Starck at low concentrations, and for other reasons, which will be considered

[1] See Bredig: *Ztschr. phys. Chem.*, 13, 202 (1894).

## Transport Numbers of Bivalent Electrolytes.

| | 1. | 2. | 5. | 10. | 16. | 20. | 25. | 50. | 100. | 200. |
|---|---|---|---|---|---|---|---|---|---|---|
| | 1. | 0.5. | 0.2. | 0.1. | 0.063. | 0.05. | 0.04. | 0.02. | 0.01. | 0.005. |
| $H_2SO_4$ | 0.175 (S) | 0.163 (S) | 0.150 (S) | 0.140 (S) | 0.135 (S) | 0.180(B) | .... | .... | .... | .... | .... |
| " | 0.177 (H) | 0.176 (W) | 0.212 (H) | 0.206 (H) | .... | .... | .... | .... | .... | .... | .... |
| $K_2SO_4$ (N) | .... | .... | 0.507 | .... | .... | .... | 0.504 | .... | .... | .... | .... |
| $BaCl_2$ | .... | 0.611 (Ho) | 0.585 (N) | 0.570 (B) | .... | 0.560 (A) | .... | 0.555 (A) | 0.550 (A) | 0.550 (A) | |
| $Ba(NO_3)_2$ (N) | .... | .... | 0.545 | .... | .... | .... | 0.544 | .... | .... | .... | .... |
| $CaCl_2$ (A) | .... | 0.66 | 0.63 | 0.62 | .... | 0.60 | .... | 0.58 | 0.56 | 0.55 | |
| $Ca(NO_3)_2$ (SD) | .... | .... | .... | .... | .... | .... | .... | .... | | 0.55 | |
| $CaSO_4$ (SD) | .... | .... | .... | .... | .... | .... | .... | .... | | 0.559 | |
| $SrCl_2$ (B) | .... | .... | .... | .... | .... | 0.575 | .... | .... | 0.555 | .... | |
| $CuSO_4$ (A) | ... | 0.670 | 0.640 | 0.630 | .... | 0.625 | .... | 0.620 | .... | .... | |
| $CdCl_2$ (A) | .... | .... | 0.61 | 0.59 | .... | 0.57 | .... | 0.56 | 0.555 | .... | |
| $CdBr_2$ (J) | 0.782 | 0.650 | 0.585 | 0.568 | .... | 0.568 | .... | 0.570 | 0.570 | .... | |
| $CdI_2$ (A) | 1.12 | 1.00 | 0.825 | 0.69 | .... | 0.62 | .... | 0.57 | 0.56 | .... | |

Note.—With the exception of the numbers in the second row under $H_2SO_4$ all are from work published since January, 1898. The results in the row mentioned (H and W) are much older determinations by Hittorf and by Wiedemann. Other letters refer to the references on page 68, as follows: (B) Bein; (Ho) Hopfgartner. (J) Jahn; (N) Noyes; (S) Starck; (SD) Steele and Denison; (A) Averages from two or more of these sources.

Some of the numbers are interpolations to correspond with the concentrations at the head of the table.

later, this value seems to be the most trustworthy for the transport number of the anion of sulphuric acid in dilute solutions. Recent results of my own, which have not yet been published,[1] confirm this value of Bein.

Jahn and Buschnewski have recently found that the transport number of $BaCl_2$ has a value practically constant (0.550) between the concentrations 0.03 and 0.005. Noyes obtained the value 0.558 at $v = 25$, and Bein 0.559 at $v = 100$. The results in the table beyond $v = 20$ are estimates from these values. Hopfgartner, working at concentrations between normal and tenth-normal, found values somewhat higher than those found by Noyes or by Bein.

For $CaCl_2$ at the concentration 0.01 Bein obtained the transport number 0.553, and at the concentration 0.005 Steele and Denison found 0.562.

The transport numbers of few compounds have been so completely investigated as those of cadmium, particularly the chloride and iodide. Unfortunately, however, the value of $A_\infty$ cannot be very accurately estimated for these substances, so that the migration number of cadmium is by no means so well fixed as might be expected. The presence of complex ions in the more concentrated solutions is illustrated in a marked manner by the conduct of cadmium iodide. Its transport number is considerably greater than 1 at concentrations greater than normal.[2] As the concentration, however, decreases from normal it is seen that the transport number rapidly decreases in value, showing that the complex ions are being decomposed. At the concentration 0.01 the transport number has become practically constant, indicating that no complex ions are present in solutions more dilute than this. The transport number of cadmium chloride behaves similarly, although in not so marked a manner. The transport numbers of other bivalent electrolytes exhibit this conduct commonly only in a slight degree.

In discussing binary electrolytes mention was made of the fact that the transport numbers of these electrolytes also undergo a change in concentrated solutions. This change is very likely

[1] Since writing this they have been published, *J. Am. Chem. Soc.*, 26, 1039 (1904). The value found in dilute solution is given by the equation, $n_t = 0.1788 + 0.0011\ (t - 20^\circ)$.

[2] See the values given by Kohlrausch and Holborn : *Leitvermögen der Electrolyte*. For a theoretical discussion of this fact see Steele and Denison : *J. Chem. Soc.*, 81, 457 (1902).

partly due to increased viscosity of the solution which affects the speed of the anion and cation differently, but for the most part it must be ascribed to the existence of complex ions here as well as in solutions of bivalent electrolytes (see page 55).

**MIGRATION NUMBERS OF BIVALENT IONS.**—On account of the variation of the transport numbers of bivalent electrolytes with the concentration, Kohlrausch's law of the independent migration of the ions had never been conclusively proved to hold true for such electrolytes until recently. Kohlrausch, in a paper published in 1898,[1] collected all the transport numbers which had been determined up to that time in dilute solutions, and pointed out that it was very probable that the law was of universal application, the errors being no greater than were to be expected from the insufficiency of the data in many cases. Very recently, however, the investigations of Noyes and of Steele and Denison have shown that it is possible to determine transport numbers quite accurately in very dilute solutions. Constant values have been obtained for the transport numbers of $BaCl_2$, $Ba(NO_3)_2$ and $CaCl_2$, and, in fact, for most of the electrolytes of the above table. These results supply additional evidence to support the law of the independent migration of the ions in its application to bivalent electrolytes and place the migration numbers of bivalent ions on a firmer foundation.

According to the most probable value of the migration number of the H ion (318 at 18°), the value $\Lambda_\infty$ for $\frac{1}{2}H_2SO_4$ cannot be far from 388. Assuming this value as a basis for computation and using Starck's smallest transport number (0.135 at $v = 16$), we obtain for the migration number of the H ion 336, which is undoubtedly too high. From Bein's value (0.180 at $v = 20$) the migration number 318 is obtained, which agrees with the above value.

From Bein's value we also find the migration number of $\frac{1}{2}SO_4$ to be 70. From Noyes' value (0.504) of the transport number of $\frac{1}{2}K_2SO_4$ at the concentration 0.04, assuming $\Lambda_\infty = 135.5$, the migration number of $\frac{1}{2}SO_4$ is found to be 68.3. Steele and Denison have calculated 68.2 for the migration number of $\frac{1}{2}SO_4$ from the transport number obtained by them for $CaSO_4$. From

[1] *Wied. Ann.*, 66, 785.

$CuSO_4$, on the assumption that $\Lambda_\infty = 118$, the migration number of $\frac{1}{2}SO_4$ is found to be 73.2. The approximate average of all these, viz., 70, was formerly adopted by Kohlrausch, as the migration number of this ion. Kohlrausch, however, in his most recent work[1] considers 68.1 the most probable value of this quantity. The migration numbers in the table below are taken from the paper of Kohlrausch and Grüneisen.

MIGRATION NUMBERS OF BIVALENT IONS.

| Anions. | | | Cations. | | |
|---|---|---|---|---|---|
| | 18°. | 25°. | | 18°. | 25°. |
| $\frac{1}{2}SO_4$.... | 68.1 | 79 | $\frac{1}{2}Ca$.... | 51.5 | 61 |
| $\frac{1}{2}C_2O_4$... | 62.6 | 69 | $\frac{1}{2}Sr$.... | 51.5 | 61 |
| | | | $\frac{1}{2}Ba$.... | 55.1 | 65 |
| | | | $\frac{1}{2}Mg$... | 45.9 | 54 |
| | | | $\frac{1}{2}Zn$.... | 46.6 | 55 |
| | | | $\frac{1}{2}Cu$.... | 47.2 | 55 |
| | | | $\frac{1}{2}Cd$.... | 47.4 | 55 |
| | | | $\frac{1}{2}Pb$.... | 61.1 | 71 |

**EFFECT OF COMPLEX IONS ON TRANSPORT NUMBERS.**—We have just seen that in all solutions of bivalent electrolytes much stronger than tenth-normal there very likely exists, besides simple ions, one or more kinds of complex ions. It has also been shown that in the behavior of solutions of strong univalent electrolytes there are certain anomalies, which can only be explained on the assumption of the presence of some sort of complex ions (see pages 55, 77). In cases then where such complex ions are present the transport numbers as determined simply represent changes in concentration around the electrodes caused by the movement of all the ions, and the effect due to any one of them cannot, in general, be estimated. Kümmell[2] has, however, recently attempted such an estimation in one of the more simple cases of this kind by means of the principles of isohydric solutions.

Solutions are isohydric when they possess a common ion having the same concentration in each solution (see, for fuller discussion, Chapter X). Whether the simple laws of isohydric solutions hold when one of the electrolytes is binary is doubtful, but Kümmell's application of the principle is so ingenious that it deserves notice.

He employed solutions of $MgCl_2$ varying in concentration from

[1] Kohlrausch and Grüneisen: *Sitzungsber. Kgl. pr. Akad. Wiss.*, Berlin, 1904, p. 1215.

[2] *Zischr. Elektrochem.*, 9, 975 (1903).

twice-normal to twentieth-normal. He assumes that at these concentrations no ions more complex than the MgCl ion are present and that the friction of the ions on one another can be neglected. The concentration of the Cl ions is then determined by finding the solution of KCl isohydric with each of the $MgCl_2$ solutions. The concentration of these ions in the latter solution is then the same as that in the former. The accompanying table exhibits the results thus obtained.

| Equivalent dilution, $v$, of $MgCl_2$ solution. | $\Lambda_v$ $MgCl_2$ at 25°. | Dilution, $v'$, of isohydric KCl solution. | Degree of dissociation of KCl. | Concentration, $c$, of Cl ions. |
|---|---|---|---|---|
| 0.5 | 56.0 | 0.60 | 0.68 | 1.133 |
| 0.668 | 63.0 | 0.806 | 0.703 | 0.872 |
| 1.0 | 69.1 | 1.215 | 0.72 | 0.593 |
| 2.0 | 77.5 | 2.434 | 0.754 | 0.310 |
| 10.0 | 99.5 | 12.2 | 0.88 | 0.0722 |
| 20.0 | 104.0 | 22.3 | 0.895 | 0.0401 |

Letting $c$ = the concentration of the Cl ions, $c_1$ of the MgCl ions and $c_2$ of the $\frac{Mg}{2}$ ions, and also letting $l_a$, $l_{c_1}$, and $l_{c_2}$ be the migration numbers of these three ions, respectively, and noting that $c_2 = c - c_1$, we then obtain

$$\Lambda_v = cvl_a + c_1vl_{c_1} + (c-c_1)vl_{c_2}. \qquad (1)$$

Substituting $l_a = 76$ and $l_{c_2} = 57$,[1] and assuming $l_{c_1} = 0$, the following values for the concentration of the MgCl ion at the different dilutions are obtained:

| $v$ = | 0.5 | 0.668 | 1 | 2 | 10 | 20 |
|---|---|---|---|---|---|---|
| $c_1$ = | 0.68 | 0.38 | 0.17 | 0.04 | 0 | 0 |

Assuming that only MgCl and Cl ions are present in the most concentrated solution, we have $c_2 = 0$ and $c_1 = c$, from which we find that $l_{c_1} = 23$. That is, the maximum value of the migration number of the MgCl ion is 23, while we may assume 0 to be its minimum value as above. Substituting then $l_{c_1} = 23$ in equation (1) we have again for the concentrations of the MgCl ions the following values:

| $v$ = | 0.5 | 0.668 | 1 | 2 | 10 | 20 |
|---|---|---|---|---|---|---|
| $c_1$ = | 1.133 | 0.649 | 0.288 | 0.073 | 0 | 0 |

The concentration of the MgCl ions at different dilutions must,

[1] These values are those used by Kümmell and are for 25°.

therefore, lie between the values found in these two tables. The two tables agree in representing the concentration of these ions at dilutions from 10 liters up as equal to zero; that is, it is highly probable that there are no MgCl ions at concentrations beyond tenth-normal.

To calculate the transport number of the anion Kümmell proceeds as follows:

For a gram-equivalent of chlorine to separate at the anode, it is necessary that there migrate from the anode

$$\frac{l_{c_1}}{l_{c_1}+l_a}\cdot\frac{a}{a+b}\text{ MgCl ions, and }\frac{l_{c_2}}{l_{c_2}+l_a}\cdot\frac{b}{a+b}\text{ Mg ions,}\quad(2)$$

in which $a$ and $b$ are partition coefficients indicating how the current is divided between the MgCl and corresponding Cl ions on the one hand and the Mg ions with their corresponding Cl ions on the other hand. At the same time there migrates to the anode

$$\frac{l_a}{l_{c_1}+l_a}\cdot\frac{a}{a+b}+\frac{l_a}{l_{c_2}+l_a}\cdot\frac{b}{a+b}\text{ Cl ions,}\quad(2)$$

and this is the transport number of the anion.

Now let us imagine the solution divided into two layers, one containing all the MgCl ions and the corresponding Cl ions and the other the Mg ions and the Cl ions corresponding to them. If $\kappa_1$ and $\kappa_2$ represent the conductivities of these two layers respectively, and $\kappa$ the total conductivity of the solution, we have $\kappa_1+\kappa_2=\kappa$. Remembering that $c=\frac{\alpha}{v}$, then

$$\kappa v\cdot 10^3=\Lambda_v=\alpha\Lambda_\infty=cv\Lambda_\infty=c_1v(l_{c_1}+l_a)+c_2v(l_{c_2}+l_a),$$

and, therefore,

$$\kappa_1=\frac{c_1(l_{c_1}+l_a)}{10^3},\quad \kappa_2=\frac{c_2(l_{c_2}+l_a)}{10^3}.$$

From these and from (2) we obtain for the transport number of the Cl ion

$$n_{Cl}=\frac{l_a}{l_{c_1}+l_a}\cdot\frac{c_1(l_{c_1}+l_a)}{c_1(l_{c_1}+l_a)+c_2(l_{c_2}+l_a)}+\frac{l_a}{l_{c_2}+l_a}\cdot\frac{c_2(l_{c_2}+l_a)}{c_1(l_{c_1}+l_a)+c_2(l_{c_2}+l_a)}=\frac{l_a(c_1+c_2)}{c_1(l_{c_1}+l_a)+c_2(l_{c_2}+l_a)}.\quad(3)$$

This is the true transport number of the anion. It differs from

the transport number actually measured for the reason that some chlorine goes to the cathode with the MgCl ions. Correcting for this the apparent transport number is

$$n'_{cl} = \frac{l_a(c_1 + c_2)}{c_1(l_{c_1} + l_a) + c_2(l_{c_2} + l_a)} - \frac{l_{c_1}}{l_{c_1} + l_a}$$

$$\frac{c_1(l_{c_1} + l_a)}{c_1(l_{c_1} + l_a) + c_2(l_{c_2} + l_a)} = \frac{l_a(c_1 + c_2) - l_{c_1}c_1}{c_1(l_{c_1} + l_a) + c_2(l_{c_2} + l_a)}. \quad (4)$$

By means of this equation, equation (1) and the transport numbers of magnesium chloride,[1] $c_1$ and $l_{c_1}$ can be calculated. From the values so obtained Kümmell judges that the migration number of the MgCl ion is approximately 10, and that the concentration of this ion, at the different dilutions cannot be far from the following:

| | | | | |
|---|---|---|---|---|
| $v$ = | 0.5 | 0.668 | 1 | 2 |
| $c_1$ = | 0.8 | 0.45 | 0.2 | 0.05 |

Noting that $c_2 = c - c_1$, and letting $\beta = \frac{c_1}{c}$ = the ratio of the complex ions to the total cations, equation (4) becomes

$$n'_{cl} = \frac{l_a - \beta l_{c_1}}{l_a + l_{c_2} - \beta(l_{c_2} - l_{c_1})}. \quad (5)$$

When $l_{c_1} < l_{c_2} - l_{c_1}$, which, from the value just found for $l_{c_1}$ and from the values in the table, page 78, is probable, the numerator decreased as $\beta$ increases relatively less rapidly than the denominator, that is, the value of the fraction increases. This signifies that the transport number of the anion increases with the formation of complex cations, or increases as the concentration of the solution increases, which is in accord with the observed facts for electrolytes of this type.

Equation (4) was derived on the assumption of complex cations being present. Steele, on the other hand, gives an expression for the transport number of an electrolyte possessing complex anions, which he derives as follows:[2]

Let $c$ be the concentration of the cation and $c'$ of the complex anion, then $c - c'$ will be that of the simple anion; and let $l_c$, $l_a$ and $l_{a'}$ be the migration numbers of the cation, the simple anion

[1] Kümmell used Hittorf's corrected values: *Ztschr. phys. Chem.*, 39, 629 (1902).
[2] *Ztschr. phys. Chem.*, 40, 729 (1902).

and the complex anion respectively. The total quantity of current passing through the electrolyte is proportional to $dl_c + (c - c')l_a + c'l_{a'}$, and that carried by the anions alone is proportional to $(c - c')l_a + c'l_{a'}$. Therefore, the migration number of the anion is

$$n = \frac{(c - c')l_a + c'l_{a'}}{dl_c + (c - c')l_a + c'l_{a'}} = \frac{dl_a + c'(l_{a'} - l_a)}{c(l_c + l_a) + c'(l_{a'} - l_a)}.$$

Let $m$ be the number of single ions into which the complex anion decomposes on complete dissociation, then the change of concentration, due to the migration of these ions, is proportional to $ml_{a'}$, and the increase in concentration on the anode is proportional to $(c - c')l_a + c'ml_{a'}$. Therefore

$$n = \frac{dl_a + c'(ml_{a'} - l_a)}{c(l_c + l_a) + c'(l_{a'} - l_a)} = \frac{l_a + \beta(ml_{a'} - l_a)}{l_c + l_a + \beta(l_{a'} - l_a)}, \quad (6)$$

in which $\beta = \frac{c'}{c}$ = the ratio of the complex anions to the total number of anions.

Since $l_{a'}$ is probably less than $l_a$, the denominator tends to become smaller as the concentration of the complex ions increases, but unless $m$ is very small $ml_{a'} > l_a$, and the numerator will increase with the concentration of the complex ions; that is, the transport number will increase as the concentration of the solution increases. This is the same as was found above for complex cations, and agrees with the actual determinations.

Equation (6) may be changed to the form

$$n = \frac{l_a + \beta(l_{a'} - l_a) + \beta l_{a'}(m - 1)}{l_a + \beta(l_{a'} - l_a) + l_c}.$$

In order that $n$ may be greater than 1, it is only necessary that $\beta l_{a'}(m - 1) > l_c$. This last will be true if either $\beta$ or $m$ are large, as is undoubtedly the case with many of the cadmium salts.

## CHAPTER VIII.

### Determination of $\Lambda_\infty$. Absolute Velocity of the Ions. Graphic Representation of Conductivity.

**DIRECT METHOD FOR THE DETERMINATION OF $\Lambda_\infty$.**—It has already been shown that as the dilution of a solution increases the equivalent conductivity also increases and tends to approach a maximum value. With strong electrolytes, especially most neutral salts, this maximum value may be estimated from actual measurements of the conductivity at high dilutions, as in the following examples:

| Potassium chloride. | | Silver nitrate. | | Barium chloride. | |
|---|---|---|---|---|---|
| $m$. | $\Lambda$. | $m$. | $\Lambda$. | $m$. | $\Lambda$. |
| 0.0005 | 128.09 | 0.0005 | 113.88 | 0.0005 | 118.3 |
| 0.0002 | 128.76 | 0.0002 | 114.56 | 0.0002 | 119.8 |
| 0.0001 | 129.05 | 0.0001 | 115.01 | 0.0001 | 120.5 |
| $\Lambda_\infty = 130.1$ | | $\Lambda_\infty = 115.8$ | | $\Lambda_\infty = 121.6$ | |

This can either be done by mathematical extrapolation, or better, by means of graphic representation as in Fig. 19 (see latter part of this chapter). In this figure it will be seen that by extending curve 1 (KCl), it would be a simple matter to find where it becomes parallel to the axis of abscissas. The ordinate at this point is the limiting value of the equivalent conductivity sought.

$\Lambda_\infty$ of the stronger acids and bases can be estimated in the same way, but with a less degree of accuracy because their true conductivity at such high dilutions is more difficult to determine (see page 47). For the great majority of acids and bases, however, recourse must be taken to the indirect method in order to estimate the value of the equivalent conductivity at infinite dilution.

**INDIRECT METHOD FOR THE DETERMINATION OF $\Lambda_\infty$.**—In the case of weak electrolytes, whose equivalent conductivity shows no indication of approaching a maximum value at the highest dilutions at which it is possible to make accurate measurements, it is impracticable to calculate $\Lambda_\infty$ in any such way as the above. For instance formic acid, the strongest of the three electrolytes whose conductivity is given on page 52, is only about 35 per cent. dissociated at a dilution of 1024 liters, and from the equivalent conductivity at that dilution, *viz.*, 49, it is clearly impossible to estimate the value at infinite dilution, *viz.*, 409.

In order to calculate $\Lambda_\infty$ in such cases some electrolyte is selected which has a common ion with the weak electrolyte, and for which $\Lambda_\infty$ can be estimated by the direct method; and from this known quantity the value required is calculated by the aid of the proper migration numbers. In the case of weak acids, for example, the sodium salts are employed because they are very completely dissociated. The chlorides of the weak bases, like ammonia, are usually selected for the same reason. By making use of the migration numbers, given in the preceding chapter, $\Lambda_\infty$ of the acids or bases themselves can then be readily calculated.

The difference between $\Lambda_\infty$ of an acid and $\Lambda_\infty$ of its sodium salt is evidently the difference between the migration numbers of H and of Na. This difference at 18° is 274.5 and at 25° is 301. Therefore, to obtain $\Lambda_\infty$ of acetic acid at 25° from 94.1, the value of $\Lambda_\infty$ of sodium acetate at the same temperature, we have $94 + 301 = 395$, which is the desired quantity. Similarly for weak alkalies, like ammonia ($NH_4OH$), we add to the value of $\Lambda_\infty$ of ammonium chloride the difference between the migration numbers of OH and Cl, which is 111 at 18° and 124 at 25°.

Ostwald[1] has pointed out that the difference between the equivalent conductivity at infinite dilution and the equivalent conductivity at any given dilution not too small is practically constant for strong electrolytes of the same class. That is, $\Lambda_\infty - \Lambda_v = d$ for salts of the same type. These constant differences for three different types of salts are given in the table below. The numbers are, of course, average values, and the accuracy of the values decreases from $d_1$ up to $d_3$.

DIFFERENCES BETWEEN $\Lambda_\infty$ AND $\Lambda_v$ AT 18° AND 25°.

| | Both ions univalent. $d_1$. | | One ion univalent and one bivalent. $d_2$. | | Both ions bivalent. $d_3$. | | |
|---|---|---|---|---|---|---|---|
| v. | 18°. | 25°. | 18°. | 25°. | 18°. | 25°. | m. |
| 10000 | 1.0 | 1.1 | 2.0 | 2.3 | 5 | 6 | 0.0001 |
| 5000 | 1.4 | 1.6 | 2.8 | 3.2 | 7 | 8 | 0.0002 |
| 2000 | 2.0 | 2.3 | 4.4 | 5.1 | 11 | 13 | 0.0005 |
| 1000 | 2.7 | 3.1 | 6.1 | 7.0 | 16 | 18 | 0.001 |
| 500 | 3.6 | 4.2 | 8.3 | 9.6 | 23 | 26 | 0.002 |
| 200 | 5.5 | 6.3 | 12.3 | 14.2 | 33 | 38 | 0.005 |
| 100 | 7.5 | 8.6 | 16.5 | 19.0 | 42 | 48 | 0.01 |
| 50 | 9.8 | 11.3 | 21.5 | 24.5 | 51 | 58 | 0.02 |

1 *Lehrbuch d. allg. Chemie.*, 2, 1, 693.

These differences can be used to calculate the value of $\Lambda_\infty$ of salts which are known to be greatly dissociated in dilute solutions, as, for instance, sodium or potassium salts. This is accomplished by determining the equivalent conductivity of such a salt at a few of the dilutions given above, most conveniently at 50, 100, 200, 500 and 1000 liters, and then adding to these values the corresponding values in the above table. The average of the values so obtained is the number sought.

$\Lambda_\infty$ of weak acids can be derived in a very similar manner from the equivalent conductivity of their sodium salts at any of the above concentrations. The equivalent conductivity is determined at several concentrations and to the values so obtained the corresponding numbers in the table are added, increased by the difference between the migration numbers of H and of Na. The proper values to add to the conductivities of the sodium salts of monobasic acids have been calculated and are given below for both 18° and 25°.

| $v$ | 10000 | 5000 | 2000 | 1000 | 500 | 200 | 100 | 50 |
|---|---|---|---|---|---|---|---|---|
| $d_\infty$, 18° | 275.5 | 275.9 | 276.5 | 277.2 | 278.1 | 280.0 | 282.0 | 284.3 |
| $d_\infty$, 25° | 302.1 | 302.6 | 303.3 | 304.1 | 305.2 | 307.3 | 309.6 | 312.3 |

To illustrate the use of these numbers the value of $\Lambda_\infty$ of benzoic acid is calculated in the accompanying table from the conductivity of sodium benzoate. The measurements were made at 25°, and, according to the figures obtained, the value of $\Lambda_\infty$ of benzoic acid at this temperature is approximately 387.

| $v$. | $\Lambda$ Sodium benzoate. | $d_\infty$. | $\Lambda_\infty$ Benzoic acid. |
|---|---|---|---|
| 50 | 74.3 | 312.3 | 386.6 |
| 100 | 77.6 | 309.6 | 387.2 |
| 200 | 79.8 | 307.3 | 387.1 |
| 500 | 81.5 | 305.2 | 386.7 |
| 1000 | 82.8 | 304.1 | 386.9 |

Kohlrausch, in a recent article, gives some variations of these methods for calculating $\Lambda_\infty$, and reference is made to his paper[1] for a more complete discussion of this subject.

**$\Lambda_\infty$ OF SOME OF THE COMMON ELECTROLYTES.** — The values of $\Lambda_\infty$ of a number of electrolytes are given in the table below. They are calculated from the most trustworthy data avail-

[1] *Wied. Ann.*, 66, 785 (1898).

able, many of them being the results of recent determinations by Kohlrausch and associates. In most cases the numbers at 25° are calculated from those at 18° by means of the temperature coefficients of Déguisne[1] or of those compiled by Kohlrausch.[2]

| | 18°. | 25°. | | 18°. | 25°. |
|---|---|---|---|---|---|
| [3]KCl..... | 130.1 | 150.1 | [3]$KNO_3$..... | 126.5 | 145.6 |
| [3]NaCl..... | 109.0 | 126.8 | [3]$NaNO_3$ ... | 105.4 | 122.3 |
| [3]LiCl ..... | 98.9 | 115.0 | [3]$NH_4NO_3$ .. | 126.2 | 145.6 |
| [3]RbCl..... | 133.0 | 153.0 | [3]$AgNO_3$ ... | 116.0 | 134.1 |
| [3]CsCl ..... | 133.6 | .... | [3]$KClO_3$ .... | 119.7 | 138.1 |
| [3]$NH_4Cl$ ... | 129.8 | 150.1 | [3]$KIO_3$ ..... | 98.5 | .... |
| [3]KBr..... | 132.3 | 152.6 | [3]KSCN .... | 121.3 | .... |
| [3]KI..... | 131.1 | 151.2 | $KC_2H_3O_2$ .. | 101.5 | 117.4 |
| [3]KF ..... | 111.3 | 129.0 | $NaC_2H_3O_2$.. | 80.4 | 94.1 |
| [3]TlCl ..... | 131.5 | .... | [3]$TlNO_3$ .... | 127.9 | .... |
| HCl ..... | 383.6 | 427.7 | KOH..... | 241.0 | 273.9 |
| $HNO_3$ .... | 380.0 | 423.2 | NaOH..... | 219.9 | 250.6 |
| $HC_2H_3O_2$.. | 353 | 395 | $NH_4OH$ ... | 240.7 | 273.9 |
| ½ $BaCl_2$ .. | 120.7 | 140.7 | ½ $K_2SO_4$... | 132.6 | 153.4 |
| ½ $SrCl_2$... | 117.1 | 136.7 | ½ $Na_2SO_4$ . | 111.5 | 130.1 |
| ½ $CaCl_2$ .. | 117.1 | 136.7 | ½ $Ba(NO_3)_2$ | 117.1 | 136.2 |
| ½ $MgCl_2$.. | 111.5 | 129.7 | ½ $Ca(NO_3)_2$ | 113.5 | 132.2 |
| ½ $ZnCl_2$ .. | 112.2 | 130.7 | ½ $CaSO_4$... | 119.6 | 140 |
| ½ $H_2SO_4$.. | 386 | 431 | ½ $ZnSO_4$... | 114.7 | 134 |
| ½ $H_2C_2O_4$. | 381 | 421 | ½ $CuSO_4$... | 115.3 | 134 |

No mention is made in the above table of any of the carbonates or of any of the trivalent electrolytes as phosphoric acid and the phosphates. Any value of $\Lambda_\infty$ that might be assigned for these substances would be very uncertain, in the former case because hydrolytic action renders it impossible to measure accurately the conductivity at high dilution, and in the latter case because the dissociation of such compounds is not well understood. On the basis of $^1/_3H_3PO_4$, $\Lambda_\infty$ of this substance is given by Foster[4] as 120.8 at 18°.

**$\Lambda_\infty$ OF ORGANIC ACIDS.**—Ostwald[5] has measured the conduc-

[1] Dissertation, Strassburg, 1895. Given by Kohlrausch and Holborn: *Leitvermögen der Elektrolyte.*

[2] *Sitzungsber. Kgl. pr. Akad., Wiss.*, Berlin, 1901, 1026. Reproduced in this book, Chapter 9.

[3] These numbers are derived from recent determination by Kohlrausch and associates: *Sitzungsber. Kgl. pr. Akad., Wiss.*, Berlin, 1899, 665; 1900, 1002; 1902, 581.

[4] *Phys. Rev.*, 8, 257 (1899).

[5] *Ztschr. phys. Chem.*, 3, 170, 241, 369 (1889); Summary, p. 418.

tivity of a great number of organic acids, and has also estimated their molecular conductivity at infinite dilution. He has found, with few exceptions, that the dibasic acids are so weak that in dissociating they conduct themselves similarly to monobasic acids. It has been shown (page 61) that succinic acid yields a constant value for the dissociation constant $k$ up to a dilution of 1,024 liters, which indicates that such acids are dissociated appreciably within this dilution into only two ions, H and HA, $H_2A$ being the formula of the acid. Exceptions to this are oxalic acid beyond a dilution of 25 liters and malonic beyond a dilution of 256 liters.

The values of $\Lambda_\infty$ of some of the more common organic acids are given below. They are derived from Ostwald's values of $\mu_\infty$ by reducing to reciprocal ohms and correcting for the migration number of the hydrogen ion, which has been adopted in this work.

$\Lambda_\infty$ OF ORGANIC ACIDS AT 25°.

| Acids. | Symbols. | $\Lambda_\infty$. | Acids. | Symbols. | $V_\infty$. |
|---|---|---|---|---|---|
| Formic | $HCHO_2$ | 409 | Benzoic | $HC_7H_5O_2$ | 387 |
| Acetic | $HC_2H_3O_2$ | 395 | Salicylic | $HC_7H_5O_3$ | 387 |
| Propionic | $HC_3H_5O_2$ | 390 | Malonic | $H_2C_3H_2O_4$ | 389[1] |
| Butyric | $HC_4H_7O_2$ | 387 | Succinic | $H_2C_4H_4O_4$ | 387[1] |
| Monochloracetic | $HC_2H_2ClO_2$ | 393 | Malic | $H_2C_4H_4O_5$ | 387[1] |
| Dichloracetic | $HC_2HCl_2O_2$ | 392 | Tartaric | $H_2C_4H_4O_6$ | 387[1] |
| Trichloracetic | $HC_2Cl_3O_2$ | 389 | Maleic | $H_2C_4H_2O_4$ | 387[1] |
| Glycollic | $HC_2H_3O_3$ | 394 | Fumaric | $H_2C_4H_2O_4$ | 387[1] |
| Lactic | $HC_3H_5O_3$ | 389 | | | |

Ostwald has called attention to the fact that $\Lambda_\infty$ of the organic acids decreases with increase of the number of atoms in the molecule. Since $\Lambda_\infty$ is made up of two constants, one the migration number of the H ion and the other of the organic anion, the migration numbers of the organic anions must decrease with the increase of the number of atoms in the molecule. This decrease finally reaches a constant value (about 20), after which further increase in the number of atoms has no effect on the speed of the ion.

Bredig[2] has found the same general principles true with regard to organic cations.

**ABSOLUTE VELOCITY OF THE IONS.**—The migration numbers

[1] This value for the dibasic acid is on the assumption of dissociation into only two ions at infinite dilution.

[2] *Ztschr. phys. Chem.*, 13, 289 (1894)

$l_a$ and $l_c$ express the velocity of the ions in terms of conductivity units. The actual velocities in centimeters per second can be obtained from these in the following manner. Since $\kappa$ is the conductivity of 1 cc. of a solution when the electromotive force is 1 volt, the equivalent conductivity, $\Lambda = \frac{\kappa}{\eta}$ or $\varphi\kappa$, may be looked upon as the conductivity of 1 cc. under like conditions, provided that a whole gram-equivalent of the substance were dissolved in 1 cc. and the substance were dissociated to the same degree as at the actual concentration $\eta$. For instance, the equivalent conductivity of a normal solution is 1000 times its specific conductivity. This is, however, the conductivity which would be obtained by bringing 1000 more carriers of the electricity into the 1 cc., provided that each carrier retained unchanged its ability to carry the current. And this again is the same as imagining that the whole gram-equivalent of the substance is dissolved in the 1 cc., but that the dissociation remains the same as in the original normal solution. By the same reasoning $\Lambda_\infty$ can be considered as the conductivity of 1 cc. containing one whole gram-equivalent entirely dissociated.

Now, since 96,580 coulombs of electricity are carried by each gram-equivalent of an electrolyte, if the whole gram-equivalent were decomposed in one second, the ions composing each molecule would have together moved 1 cm. and the conductivity would be 96,580. But the conductivity under these conditions is only $\Lambda_\infty$, and, therefore, a gram equivalent has traveled only $\frac{\Lambda_\infty}{96580}$ cm. and each ion has traveled separately $\frac{l_a}{96580}$ cm. and $\frac{l_c}{96580}$ cm. This gives for the velocity of the anion,

$$0.000010354 \cdot l_a \text{ cm. per second,}$$

and for the velocity of the cation,

$$0.000010354 \cdot l_c \text{ cm. per second,}$$

when the electromotive force is 1 volt.

These expressions give the velocities of the ions in solutions sufficiently dilute so that their friction on one another can be neglected. This has been shown to be the case when the concentration does not exceed tenth-normal.

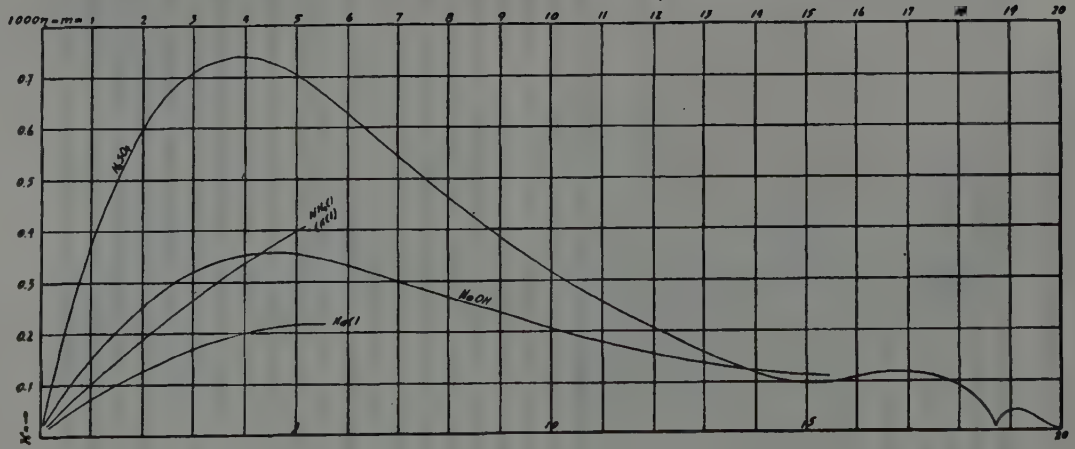
VELOCITIES OF IONS UNDER THE INFLUENCE OF AN ELECTROMOTIVE FORCE OF ONE VOLT.

| Anions. | Centimeters per second. | Cations. | Centimeters per second. |
|---|---|---|---|
| $Cl$ | 0.000679 | $K$ | 0.000668 |
| $NO_3$ | 0.000642 | $Na$ | 0.000449 |
| $C_2H_3O_2$ | 0.000383 | $Ag$ | 0.000559 |
| $OH$ | 0.00183 | $H$ | 0.00329 |

The velocities of some of the principal ions at 18° are given in the accompanying table. The extreme smallness of these velocities is due to the great resistance offered by the water, that is, the friction of the ions on the water molecules. Anything which tends to decrease this friction will increase the velocity of the ions, as, for instance, raising the temperature of the solution. Mixing alcohol with water increases the viscosity of the water and consequently the friction on ions moving through it. This is the principal reason why the conductivity of solutions to which a little alcohol has been added is diminished.

**GRAPHIC REPRESENTATION OF CONDUCTIVITY.**—The conductivity of an electrolyte may be given simply in a table in which opposite either the percentage content or the concentration is placed the corresponding specific conductivity. For most purposes, however, a knowledge of the equivalent conductivity is preferred. This latter is, therefore, more commonly given in tables than the specific conductivity. (See tables in appendix). The specific conductivity can be readily obtained from such a table, when desired, by simply multiplying the equivalent conductivity by the concentration expressed in gram-equivalents per cubic centimeter.

In many cases, however, a graphic representation is very desirable, for one can see at a glance the general trend of the conductivity, and it also affords an excellent means for accurate interpolation. By such a method conductivity is represented in the form of a curve on coordinate paper, employing the concentration or dilution as abscissas and the specific or equivalent conductivity as ordinates. By using the specific conductivity the changes which the conductivity undergoes with change of concentration are best brought out, as, for instance, in the case of sulphuric acid (Fig. 18). Here the curve shows very readily the various maxima and minima of the conductivity.


1000 n = m =
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0.7
0.6
0.5
0.4
0.3
0.2
0.1
NaCl
NaOH
HCl
5
10
15
20

Fig. 18.

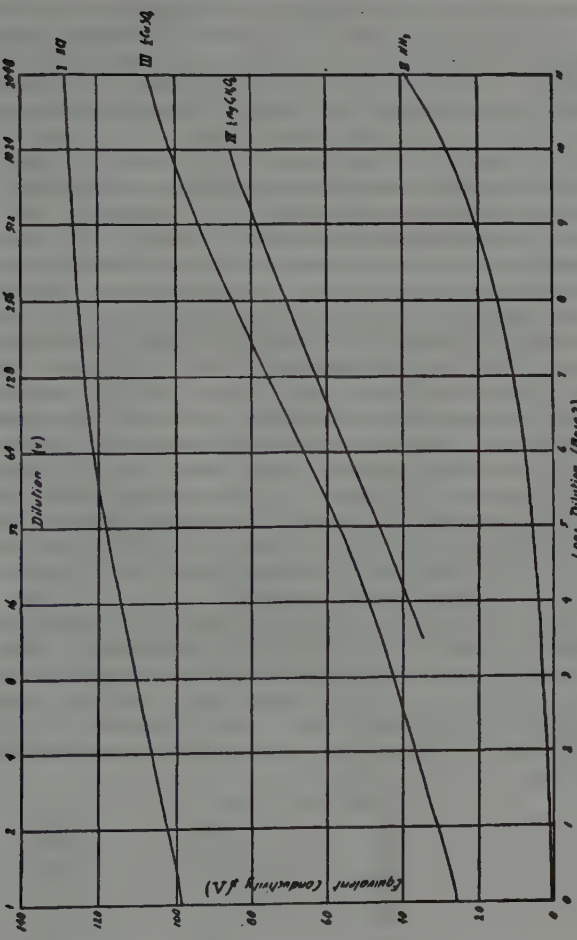


FIG. 19.

When there are no such changes to be emphasized the curve of the equivalent conductivity is usually given. Under these conditions, however, when the concentrations are used as abscissas that part of the curve representing the conductivity of the more dilute solutions is so shortened as to give but little idea of any detail and to preclude entirely interpolation. If the dilution $v$ is substituted the same is true of the more concentrated solutions. In order to overcome this difficulty the cube root of the concentration may be employed instead of the simple concentration.

Since, however, the dilutions at which the conductivity is measured are very frequently powers of 2, an excellent form of curve is obtained by using as abscissas the logarithms of the dilutions to the base 2. When plotted according to this method curves representing the conductivity of moderately dissociated electrolytes approach very closely to straight lines, while the curvature in the case of any electrolyte is not very pronounced. Fig. 19 illustrates conductivity represented in this manner. At the top of the figure are given the actual dilutions and at the bottom the logarithms (base 2) of these dilutions. Strong electrolytes yield curves similar to that of KCl (curve I), weak electrolytes like that of $NH_4OH$ (curve II), and moderately dissociated electrolytes like tnat of $\frac{1}{2}CuSO_4$ (curve III). The curves representing the conductivity of strong electrolytes are concave downward, while those of weak electrolyes are concave upward.

In order to obtain the logarithm of a number to the base 2, the Briggs' logarithm of the number must be multiplied by 3.3219. Some of the logarithms of this system, which are most helpful in plotting conductivity curves, are given below. From these other numbers which are required can be readily calculated. For instance, log. $50 = \log. 5 + \log 10$; log. $100 = 2 \times \log. 10$; log. $200 = 2 \times \log. 10 + 1$, etc.

LOGARITHMS TO BASE 2.

| Number. | Log. | Number. | Log. |
|---|---|---|---|
| 1 | 0.000 | 6 | 2.585 |
| 2 | 1.000 | 6⅔ | 2.737 |
| 3 | 1.585 | 7 | 2.807 |
| 3⅓ | 1.737 | 8 | 3.000 |
| 4 | 2.000 | 9 | 3.170 |
| 5 | 2.322 | 10 | 3.322 |

If the conductivity of an electrolyte is given at the dilutions usually employed by Kohlrausch and his associates, *viz.*, 1, 2, 5, 10, 20, 50, etc., liters, or 1; 2, 3.33, 5, 6.67, 10, 20, 33.3, etc., liters, the curve cannot be plotted quite so readily as when the dilutions are powers of 2, but with the logarithms given above no great difficulty will be experienced even in such cases. This method is especially applicable when one desires to find, by interpolation, the conductivity at the dilutions, 2, 4, 8, 16, etc., liters from determinations made with any solution of known strength by continually doubling the dilution. The method will be illustrated by the results obtained with a solution of magnesium tartrate containing at first a gram-equivalent in 11.24 liters.

EQUIVALENT CONDUCTIVITY OF MAGNESIUM TARTRATE AT 18°.

| Actual determinations. | | Interpolated values. | |
|---|---|---|---|
| *v.* | *Λ.* | *v.* | *Λ.* |
| 11.24 | 34.3 | 16 | 38.3 |
| 2 × 11.24 | 42.2 | 32 | 46.4 |
| 4 × 11.24 | 50.5 | 64 | 54.9 |
| 8 × 11.24 | 58.9 | 128 | 63.0 |
| 16 × 11.24 | 67.0 | 256 | 71.0 |
| 32 × 11.24 | 74.5 | 512 | 78.7 |
| 64 × 11.24 | 82.6 | 1024 | 86.6 |

The logarithm of 11.24 to base 2 is found by multiplying its Briggs' logarithm, 1.0508, by 3.3219, which gives 3.491. The logarithm of 2 × 11.24 is 4.491, etc. From the data thus obtained curve IV. Fig. 19, was plotted. The interpolated values given in the above table are obtained from the points where the abscissas 16, 32, 64, etc., cut this curve.

## CHAPTER IX.

### Influence of Temperature and Pressure.

**THERMOSTAT.**—The conductivity of solutions varies considerably with the temperature, increasing about 2 per cent. for a rise of 1°. It is consequently very necessary that the temperature of an electrolyte be controlled accurately while its conductivity is being measured. This is best accomplished by means of a bath, unless it is desired to make the measurements at room temperature, in which case it can be dispensed with provided the current is not passed long enough to change the temperature of the liquid in the cell.

The most suitable liquid for a bath is water, both on account of its great specific heat and its cleanliness. Paraffin oil has the advantage over water as a bath liquid in being a non-conductor, but in the respects just mentioned it is far inferior to water and hence but seldom employed. A bath should have a considerable

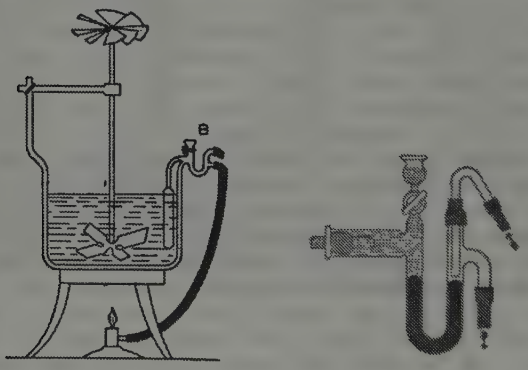


Fig. 20.

size, capable of holding 10 liters or more, since it is much easier to control the temperature of a large body of water than of a smaller one.

A bath is best kept at a temperature only 1° or 2° above that of the room by means of radiation from some warm body or by careful addition of small quantities of warm water, either by hand or preferably by means of a slowly flowing continuous current. For temperatures from 5° to 50° above room temperature the form of thermostat described by Ostwald[1] is very serviceable. It is shown in Fig. 20. The gas flame is automatically regulated by the apparatus at *B*, which is shown in increased size in *b*. The expansion of the liquid in the bulb at the bottom of the bath forces the mercury up against the mouth of the gas tube, thus regulating the flow of gas. A pin hole just above the mouth of the gas tube allows enough gas to pass, so that the flame is never entirely extinguished. Either alcohol or a 10 per cent. solution of calcium chloride may be used as the expansive liquid in the bulb. The bath is commonly stirred by means of a wind-mill stirrer, which can be operated by hot air from a Bunsen burner.

All baths should be stirred, and the greater the difference in temperature between the bath and the room the more active should be the stirring. If this difference exceeds 10° the stirrer should be driven rapidly by means of an electric or a water motor, as one operated by hot air is hardly adequate. A temperature below that of the room can be best secured by running a stream of faucet water—or if this is not cool enough, a stream of water artificially cooled—through the bath, care being taken to regulate the flow so that the temperature will remain constant. A temperature of 0° is very easy to maintain by cooling the bath with ice.

Covering the outside of a thermostat with felt, decreases radiation and hence permits keeping the temperature more nearly constant. Radiation can be somewhat hindered by using a bath which is rather deep in proportion to its diameter, so as to leave exposed comparatively little water surface. Little is accomplished by covering a shallow bath of considerable diameter with felt. If a still higher degree of constancy of temperature is required a thermostat devised by Bradley and Browne[2] is recommended. Its efficiency consists in employing an extremely sensitive regu-

[1] *Ztschr. phys. Chem.*, **2**, 565 (1888).
[2] *J. Phys. Chem.*, **6**, 118 (1902).

lator to control the flow of water, the temperature of which is regulated in a reservoir in a manner very similar to that used in the Ostwald thermostat. A constancy of temperature within a few thousandths of a degree can thus be attained.

**STANDARD THERMOMETER SCALE.**—All accurate conductivity measurements should be given for standard temperature referred to the scale of the hydrogen thermometer. The following are the corrections to be applied to an accurate mercury thermometer to reduce the readings to the hydrogen scale. The numbers are to be subtracted.

| For thermometers of Jena glass. | 0°. | 5°. | 10°. | 15°. | 18°. | 20°. | 25°. | 30°. | 35°. | 40°. | 45°. | 50°. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| No. 16 (normal) | 0 | 0.03 | 0.06 | 0.08 | 0.09 | 0.09 | 0.10 | 0.11 | 0.12 | 0.12 | 0.12 | 0.12 |
| No. 59 .. | 0 | 0.01 | 0.02 | 0.03 | 0.03 | 0.04 | 0.04 | 0.04 | 0.04 | 0.03 | 0.03 | 0.03 |

Calibration tables from the Reichsanstalt include these corrections. They have also recently been taken into consideration by some makers in dividing the thermometer scale.

**TEMPERATURE COEFFICIENTS.**—If it is desired to find the conductivity of a substance at one temperature from measurements made at some other temperature, it is necessary to know the change in conductivity of the substance per degree of temperature. This is called the temperature coefficient of the substance. For nearly all salt solutions the temperature coefficients vary from 0.021 to 0.024, for caustic alkalies from 0.019 to 0.021, and for acids and some acid salts they have still smaller values.

The temperature coefficient $c$ is found by determining the conductivity of a substance at two temperatures, $t_1$ and $t_2$, not too far apart. Since 18° is considered the standard temperature for conductivity measurements, we have

$$c = \frac{1}{\kappa_{18}} \frac{\kappa_2 - \kappa_1}{t_2 - t_1}.$$

This is called the mean temperature coefficient at $\frac{t_1 + t_2}{2}$ expressed in terms of the conductivity at 18°. The expression is of

value only for calculating the conductivity in the vicinity of the temperature $\frac{t_1 + t_2}{2}$. To compute the conductivity at such a temperature $t$, we employ the equation,

$$\kappa_t = \kappa_{18}[1 + c(t-18)],$$

or *vice versa*, to obtain the conductivity at 18° from that at $t$,

$$\kappa_{18} = \frac{\kappa_t}{1 + c(t-18)}.$$

In determining temperature coefficients, 18° is usually taken as one of the two temperatures, $t_1$ or $t_2$.

These temperature coefficients can, of course, be applied equally well to the equivalent conductivity or to the specific conductivity.

**Influence of the Concentration.**—The temperature coefficients of salts and alkalies vary but little with the concentration, that of acids much more. The variation in the case of sulphuric and phosphoric acids is so great that it should always be considered.

The following results, taken from the work of Arrhenius,[1] serve to illustrate the change in some typical temperature coefficients between the concentrations 0.001 and 0.5. The coefficients hold midway between 18° and 52°, that is, at 35°. The figures represent 10,000$c$.

TEMPERATURE COEFFICIENT:

$$c_{18} = \frac{1}{\kappa_{18}} \frac{\kappa_{52} - \kappa_{18}}{34}.$$

| 1000$\eta$ = $m$ = | 0.001. | 0.01. | 0.1. | 0.5. |
|---|---|---|---|---|
| KCl .... | 233 | 232 | 228 | 218 |
| KI ..... | 231 | 225 | 221 | 207 |
| $KNO_3$ ... | 222 | 223 | 220 | 218 |
| NaCl .... | 253 | 254 | 246 | 241 |
| $NaC_2H_3O_2$ | 268 | 274 | 261 | 271 |
| NaOH ... | ... | 213 | 202 | 202 |

| 1000$\eta$ = $m$ = | 0.001. | 0.01. | 0.1. | 0.5 |
|---|---|---|---|---|
| ½ $BaCl_2$. | 250 | 248 | 244 | 225 |
| ½ $MgCl_2$ | 254 | 253 | 248 | 243 |
| ½ $CuSO_4$ | 256 | 226 | 198 | 198 |
| HCl..... | 163 | 158 | 153 | 152 |
| $HNO_3$ ... | 154 | 152 | 147 | 143 |
| ⅓ $H_3PO_4$ | 154 | 140 | 88 | 78 |

**Influence of Temperature.**—The coefficients vary also with the temperature to a certain extent. The results below are from the work of Schaller,[2] and they were obtained with solutions at a dilution of 1024 liters. The coefficients have been multiplied by 10,000.

[1] *Ztschr. phys. Chem.*, 4, 96 (1889).
[2] *Ztschr. phys. Chem.*, 28, 497 (1898).

TEMPERATURE COEFFICIENT:

$$c_{\frac{1}{2}(25+t)} = \frac{1}{\kappa_{25}} \frac{\kappa_t - \kappa_{25}}{t-25}.$$

| ½ (25 + t). | KCl. | NaCl. | $KNO_3$. | $NaNO_3$. | HCl. |
|---|---|---|---|---|---|
| 32.5° | 207.1 | 215.8 | 201.0 | 208.4 | 141.0 |
| 37.5 | 206.9 | 217.5 | 202.7 | 213.6 | 139.2 |
| 42.5 | 210.5 | 220.2 | 204.7 | 217.4 | 135.4 |
| 47.5 | 213.0 | 223.7 | 207.0 | 219.1 | 132.0 |
| 52.5 | 215.2 | 226.5 | 209.0 | 220.3 | 128.3 |
| 57.5 | 216.2 | 229.7 | 208.8 | 221.6 | 125.0 |
| 62.0 | 216.7 | 231.9 | 209.3 | 225.1 | 123.2 |

Here again the temperature coefficients of the acids seem to show the greatest changes. The coefficients of the salts increase with the temperature, while those of the acids decrease. At higher temperatures, however, the coefficients of salts also decrease.

**Quadratic Equations for Temperature Reduction.**—Since the coefficients themselves vary thus with the temperature, in reducing conductivity determinations from one temperature to another, a quadratic equation is better adapted to yield accurate results than a simple linear equation like the above. Such a quadratic equation has the form

$$\kappa = \kappa_0[1 + c(t-t_0) + c'(t-t_0)^2],$$

in which 18° is usually taken as $t_0$.

In order to evaluate both $c$ and $c'$ in the above equation the conductivity must be known at three different temperatures, that is, the conductivities $\kappa_0$, $\kappa_1$, and $\kappa_2$ at the temperature $t_0$, $t_1$ and $t_2$. From these we are able to obtain the two equations:

$$\frac{1}{\kappa_0} \frac{\kappa_1 - \kappa_0}{t_1 - t_0} = c + c'(t_1 - t_0), \qquad (a)$$

$$\frac{1}{\kappa_0} \frac{\kappa_2 - \kappa_0}{t_2 - t_0} = c + c'(t_2 - t_0). \qquad (b)$$

Subtracting *(a)* from *(b)*,

$$c' = \frac{1}{t_2 - t_1} \frac{1}{\kappa_0} \left( \frac{\kappa_2 - \kappa_0}{t_2 - t_0} - \frac{\kappa_1 - \kappa_0}{t_1 - t_0} \right). \qquad (c)$$

By substituting then the value of $c'$ in either $(a)$ or $(b)$ $c$ can be readily determined. In order to secure the greatest accuracy the temperatures should be chosen so that $t_1$ lies midway between

$t_0$ and $t_1$. Déguisne[1] has determined the values of $c$ and $c'$ for a number of electrolytes. The temperature coefficients of the acids, as has been said, vary considerably with the concentration, Déguisne's results with the principal acids are therefore given below.

VALUES OF $c$ AND $c'$ IN THE FOLLOWING EQUATION:

$$\kappa_t = \kappa_{18}[1 + c(t-18) + c'(t-18)^2].$$

| | HCl. | | $HNO_3$. | | $\frac{1}{2}H_2SO_4$. | | $\frac{1}{3}H_3PO_4$. | |
|---|---|---|---|---|---|---|---|---|
| m. | $10^4c$. | $10^6c'$. | $10^4c$. | $10^6c'$. | $10^4c$. | $10^6c'$. | $10^4c$. | $10^6c'$. |
| 0.00005 | 172.4 | 1.5 | 169.2 | 6.2 | 166.9 | 12.8 | 206.6 | 75.6 |
| 0.0001 | 166.0 | 9.2 | 164.7 | 14.7 | 166.9 | 12.8 | 174.2 | 6.8 |
| 0.001 | 164.2 | 15.5 | 163.0 | 14.4 | 158.1 | 36.2 | 158.8 | 28.1 |
| 0.01 | 164.1 | 17.3 | 161.7 | 19.4 | 130.8 | 101.5 | 146.3 | 61.6 |
| 0.05 | .... | ... | .... | ... | .... | .... | 136.3 | 78.2 |

Kohlrausch[2] has recently tabulated a considerable number of temperature coefficients in the order of their magnitude and has derived therefrom some interesting relations. His table is reproduced below. The coefficients are to be used in the same equation as that given in the preceding table. They hold for solutions of a concentration of about 0.001.

| Electrolyte. | $10^4c$. | $10^6c'$. | Electrolyte. | $10^4c$. | $10^6c'$. |
|---|---|---|---|---|---|
| $HNO_3$ ..... | 163 | 16 | $K_2SO_4$ ..... | 222 | 77 |
| HCl ..... | 164 | 15 | $Pb(NO_3)_2$ ..... | 224 | 78 |
| $H_2SO_4$ ..... | 165 | 17 | $BaCl_2$ ..... | 225 | 83 |
| $H_3PO_4$ ..... | 169 | 1 | NaCl ..... | 226 | 84 |
| KOH ..... | 190 | 32 | $SrSO_4$ ..... | 228 | 84 |
| $KNO_3$ ..... | 210 | 62 | $Na_2SO_4$ ..... | 233 | 97 |
| KI ..... | 212 | 58 | $MgSO_4$ ..... | 238 | 95 |
| $AgNO_3$ ..... | 216 | 67 | $NaHC_4H_4O_4$ .... | 241 | 109 |
| KCl ..... | 217 | 67 | NaF ..... | 242 | 102 |
| $NH_4Cl$ ..... | 219 | 68 | $NaC_2H_3O_2$ ..... | 242 | 110 |
| $NaNO_3$ ..... | 220 | 75 | $NaC_3H_5O_3$ ..... | 243 | 111 |
| $Ba(NO_3)_2$ ..... | 220 | 75 | $Na_2CO_3$ ..... | 262 | 151 |
| KF ..... | 222 | 79 | | | |

It is seen that as $c$ increases $c'$ also increases, and within the limits of experimental error the following relation holds:

$$c' = 0.0163\ (c - 0.0174).$$

Since, therefore, $c'$ can be calculated from $c$, the change of conductivity with the temperature may be expressed by a single ar-

[1] Dissertation, Strassburg, 1895. Déguisne's results are given in full by Kohlrausch and Holborn: *Leitvermögen der Elektrolyte.*

[2] *Sitzungsber. Kgl. pr. Akad. Wiss.*, Berlin, 1901, p. 1026.

bitrary constant. If the above equation holds, at about —39° all aqueous solutions of electrolytes lose their conductivity. Kohlrausch infers that this may very likely be true, since this is also the temperature at which water loses its fluidity, according to the generally accepted equation for the coefficient of viscosity:

$$\eta = 2.989(t + 38.5)^{-1.40} \text{ in C. G. S. units.}$$

It is unfortunately impossible to verify this conclusion with dilute solutions at such low temperatures. Kunz[1] has, however, attempted a verification with concentrated solutions of sodium hydroxide, calcium chloride, and sulphuric acid. His results with 60.9 per cent. $H_2SO_4$ follow:

| Temperature. | 0°. | —10.5°. | —20.3°. | —33.4°. | —51.9°. | —69.9°. |
|---|---|---|---|---|---|---|
| 1000κ | 232 | 171 | 124 | 71.9 | 19.4 | 1.31 |

In concentrated solutions, therefore, Kohlrausch's conclusion seems not to be upheld. But it is hardly a satisfactory test to attempt to support a relation derived from the conduct of 0.001 normal solutions by facts obtained by working with solutions 10,000 times more concentrated. Kunz concludes that conductivity decreases as the temperature is lowered on account of the increasing viscosity of the medium in which the ions move, and that conductivity only ceases at the absolute zero.

The data on temperature coefficients has been recently added to also by Foster,[2] and by Jones and Douglas.[3] The former has determined the coefficients of a number of normal solutions. Jones and Douglas have determined the conductivity of many acids, bases, and salts at four temperatures, from 0° to 35°, and at dilutions varying, in general, from 1 to 2048 liters, but have only partially reduced the data thus obtained (see appendix, Table V).

**TEMPERATURE COEFFICIENTS AT HIGH TEMPERATURES.**— In the case of most aqueous solutions the temperature coefficients first increase with rise of temperature, then decrease. Arrhenius[4] has deduced from theoretical considerations that at high temperatures the coefficients continue to decrease with rise of temperature until they become zero, after which they become negative. Or

[1] *Compt. Rend.*, 138, 788 (1902); also *Ztschr. phys. Chem.*, 42, 593 (1903).
[2] *Phys. Rev.*, 8, 257 (1899).
[3] *Am. Chem. J.*, 26, 428 (1901).
[4] *Ztschr. phys. Chem.*, 4, 96 (1889).

what amounts to the same, the conductivity increases with the temperature, reaches a maximum and then decreases. He was able to verify this for solutions of hypophosphorous acid and phosphoric acid, the maximum conductivity of the former being at about 55° and of the latter at 75°. Since then maxima of conductivity have been found for solutions of copper sulphate and of a number of organic acids. The maximum conductivity of most aqueous solutions, however, lies so high that the experimental difficulties have prevented the verification of the Arrhenius theory for any considerable number of electrolytes. In many cases it has been predicted that this point lies even higher than the critical temperature of water.

The change in conductivity of a solution with the temperature may be due primarily to two causes: change in the speed of the ions, and change in the degree of dissociation. At high temperatures the degree of dissociation seems to decrease to counteract the heating effect,[1] and at a certain point this influence overcomes the tendency of the ions to move faster on account of the diminished viscosity of the water, so that at temperatures above this the conductivity falls off until at the critical temperature it becomes very small, almost zero in many cases. This last is contrary to predictions which have been ventured on the basis of the Arrhenius theory, but it seems to be supported by some of the most careful measurements with non-aqueous solutions,[2] where, on account of the low critical temperature of many solvents, experimental verification is possible.

**REDUCTION OF CONDUCTIVITY MEASUREMENTS FOR SMALL TEMPERATURE DIFFERENCES.**—When only a few conductivity measurements are to be made, in order to save time required to adjust a temperature bath at 18°, the measurements may be made at room temperature, care being exercised to take the temperature of the solution at the instant when the measurements are made. Subsequently, the results can be reduced to 18° by means of the coefficients given on page 99. If the temperature interval is slight the temperature coefficient $c$ can be employed alone without sensible error.

[1] That is, recombination of the ions at these temperatures absorbs heat.

[2] See Eversheim: *Drud. Ann.*, 8, 560 (1902); Walden and Centnerszwer: *Ztschr. phys. Chem.*, 39, 538 (1902), and also discussion in Chapter 12.

For example, a tenth-normal solution of silver nitrate gave $\kappa = 0.00793$ at 19.32°. The temperature coefficient $c$ of silver nitrate in the table is in round numbers 0.022. Since the difference of temperature here is only 1.32°, the use of this approximate coefficient will cause no appreciable error. Employing the formula

$$\kappa_{18} = \frac{\kappa_t}{1 + c(t-18)},$$

we have

$$\kappa_{18} = \frac{0.00793}{1 + 0.022 \times 1.32} = \frac{0.00793}{1.029} = 0.00771.$$

By means of the same coefficients the equivalent conductivity at one temperature may also be calculated from that at some other temperature not too remote.

**INFLUENCE OF PRESSURE ON CONDUCTIVITY.**—The effect of an increase of pressure on the conductivity of electrolytes has been investigated by Fanjung,[1] Tammann,[2] and Bogojawlensky and Tammann.[3] It might be conjectured *a priori* that an increase of pressure would increase the friction of the particles in solution and consequently decrease the conductivity. Such, however, is not the case, for the conductivity increases with the pressure. As Tammann points out in his latest investigation where he employed pressures up to more than 3500 atmospheres on both strong and weak electrolytes, this behavior is due to two causes: First, contrary to the conduct of most liquids the viscosity of water and its dilute solutions decreases with increase of pressure. This decrease of the viscosity causes the ions to move more rapidly. Secondly, the dissociation of electrolytes in solution in distinction from the dissociation of gases is accompanied by a contraction of volume. An increase of pressure is, therefore, favorable to this and increases the dissociation of the electrolyte.

Tammann's results with tenth-normal solutions of sodium chloride and of acetic acid, one an example of strong electrolytes and the other of weak, are given below. The pressure is given in kilograms per square centimeter, and in the column headed $\frac{R_p}{R_1}$

[1] *Ztschr. phys. Chem.*, 14, 673 (1894).
[2] *Ibid.*, 17, 725 (1895), and also *Wied. Ann.*, 69, 767 (1899).
[3] *Ztschr. phys. Chem.*, 27, 457 (1898).

is given the ratio of the electrical resistance of the electrolyte at the pressure $p$ to the resistance at the pressure unity. The measurements were made at 0°.

| Pressure. | $N/10$-NaCl. $\frac{R_p}{R_1}$. | $N/10$-$C_2H_4O_2$. $\frac{R_p}{R_1}$. |
|---|---|---|
| 1 | 1.000 | 1.000 |
| 500 | 0.925 | 0.855 |
| 1000 | 0.889 | 0.734 |
| 1500 | 0.869 | 0.644 |
| 2000 | 0.858 | 0.582 |
| 2500 | 0.854 | 0.526 |
| 3000 | 0.855 | 0.487 |
| 3500 | 0.857 | 0.460 |
| 4000 | 0.858 | 0.430 |

Since the conductivity varies inversely as the resistance, the conductivity of the well dissociated electrolyte, sodium chloride, is found to increase much less with the pressure than that of the weak electrolyte, acetic acid. Tammann ascribes this to the fact that the second of the above influences is not operative to an appreciable extent in the case of a dilute solution of sodium chloride, while it is in the case of a dilute solution of acetic acid. That is, the contraction in volume of the acetic acid solution is much greater with increase of pressure than that of the sodium chloride solution. Fanjung found that the conductivity of a solution containing an electrolyte in such concentration that it was practically completely dissociated also increased with the pressure. The first of the causes mentioned above is, of course, the only one which can be active in such a case and the increase in conductivity is due to the more rapid movement of the ions. To draw the conclusion from this, however, that in every case the increase in conductivity, due to increased pressure, is caused simply by an increased velocity of the ions and not by increased dissociation, is entirely unwarranted.

As to the effect of changing the temperature, Tammann found by investigation at 20° and 40°, as well as at 0°, that the higher the temperature the less the increase in the conductivity with increase of pressure in the case of the tenth-normal solution of sodium chloride, but that in the case of the solution of acetic acid change of temperature has but little influence on the effect of the pressure in changing the conductivity.

## CHAPTER X.

### Solutions Containing Two Electrolytes.

**ISOHYDRIC SOLUTIONS.**—In considering a solution containing two electrolytes it is usually convenient to assume that it has been formed by mixing two solutions, each one of which contains only one electrolyte. The simplest conditions then prevail between the conductivity of the mixture and the conductivities of the two component solutions when the latter are **isohydric**[1], that is, the component solutions possess a common ion in equal concentration. This is true when

$$\frac{\alpha_1}{v_1} = \frac{\alpha_2}{v_2},$$

in which $\alpha_1$ is the dissociation of one of the electrolytes at the dilution $v_1$, and $\alpha_2$ is the dissociation of the other at the dilution $v_2$. A fifth-normal solution of acetic acid is isoyhdric with a 450th-normal solution of hydrochloric acid, because the concentration of the hydrogen ions in the two solutions is equal. Such solutions can be mixed in any proportion without altering their dissociation, and hence the conductivity of the mixture is the mean of the conductivities of the separate solutions and can, therefore, be calculated according to the following formula:

$$\kappa = \frac{\kappa_1 A + \kappa_2 B}{A + B},$$

in which $\kappa_1$ and $\kappa_2$ are the conductivities and $A$ and $B$ the proportions of the component solutions.

A single case, in which this last formula applies, is not sufficient proof that two solutions are isohydric. Solutions are only proved to be isohydric when, mixed in several quite different proportions, this formula gives the correct conductivity in each case. This is illustrated by the following examples taken from the work of Hofmann.[2]

[1] Arrhenius: *Wied. Ann.*, 30, 51 (1887); *Ztschr. phys. Chem.*, 2, 284 (1888).
[2] *Ztschr. phys. Chem.*, 43, 584 (1903).

ISOHYDRIC SOLUTIONS.

| | $\kappa$ measured. | $\kappa$ calculated. |
|---|---|---|
| 3.22-normal HCl | $\kappa_1 = 0.7441$ | ..... |
| 3.32-normal HBr | $\kappa_2 = 0.7504$ | ..... |
| 1 vol. HCl + 1 vol. HBr | 0.7465 | 0.7472 |
| 1 " HCl + 3 " HBr | 0.7489 | 0.7488 |
| 3 " HCl + 1 " HBr | 0.7470 | 0.7457 |

NON-ISOHYDRIC SOLUTIONS.

| | $\kappa$ measured. | $\kappa$ calculated. | Deviation. Per cent. |
|---|---|---|---|
| 3.22-normal HCl | $\kappa_1 = 0.7441$ | ..... | .. |
| 2.05-normal $H_2CrO_4$ | $\kappa_2 = 0.2382$ | ..... | .. |
| 1 vol. HCl + 1 vol. $H_2CrO_4$ | 0.4909 | 0.4911 | 0.0 |
| 1 " HCl + 3 " $H_2CrO_4$ | 0.3479 | 0.3647 | −4.6 |
| 3 " HCl + 1 " $H_2CrO_4$ | 0.6395 | 0.6176 | +3.5 |

If only the conductivity of the first mixture of the HCl and $H_2CrO_4$ solutions had been measured, one might easily have been misled into considering them isohydric. The conductivity of the last two mixtures, however, shows this to be far from the case.

**COMPONENT SOLUTIONS NOT ISOHYDRIC; WAKEMAN'S INVESTIGATION.**—When the component solutions are not isohydric the conditions are much less simple than above. The simplest case of this kind is where both electrolytes have a common ion and each obeys the law of mass-action in its dissociation, that is, is a weak electrolyte. In a case of this kind, although the solutions actually mixed are not isohydric, the mixture can be imagined to be formed from two solutions of the same electrolytes which are isohydric. The difficulty, however, arises in ascertaining the unknown concentrations of such isohydric solutions of the components. Various algebraic expressions have been derived to meet the requirements of such cases, notably by Arrhenius and by van Laar, but on account of the number of unknown quantities involved they can be solved only by approximation.

Wakeman[1] has shown that in certain simple cases the concentrations of the isohydric solutions of the components can be found without much difficulty by trial.

He mixed equal volumes of a 0.3117-normal acetic acid solution ($v_1 = 3.208$) and of a 0.004156-normal cyanacetic acid solution ($v_2 = 240.6$). A gram-molecule of the two together was, there-

[1] *Zischr. phys. Chem.*, 18, 159 (1894).

fore, contained in 6.331 liters. The value of the constant of the Ostwald formula for these acids is $k_1$[1] $= 0.000018$ and $k_2 = 0.0037$. The degree of dissociation at the dilutions $v_1$ and $v_2$ are $\alpha_1 = 0.00757$ and $\alpha_2 = 0.5984$.

If the solutions first mixed were isohydric,

$$\frac{\alpha_1}{v_1} = \frac{\alpha_2}{v_2}.$$

But

$$\frac{\alpha_1}{v_1} = \frac{0.00757}{3.208} = 0.002360, \text{ and } \frac{\alpha_2}{v_2} = \frac{0.5984}{240.6} = 0.002487.$$

Consequently these solutions were not isohydric.

We can now imagine for a moment that the solution of the mixed electrolytes is separated into two equal parts, one superimposed upon the other, and each part containing a single electrolyte. Then, since the original acetic acid solution contained 75 times as many mols[2] per liter as the original cyanacetic acid solution, 75/76 mol acetic acid would be in the upper half in 3.1655 litres, and 1/76 mol cyanacetic acid in the lower half in the same volume. Now the concentration of hydrogen ions is greater in the lower solution, so we can imagine water to pass from the upper acetic acid layer into the lower cyanacetic acid layer, until the concentration of the hydrogen ions has become equal. The change of dilution required cannot, however, be calculated directly from the difference in concentration of the hydrogen ions at the beginning, because as the solutions become stronger or weaker the degree of dissociation also changes, thereby complicating the process.

However, the required change of concentration can be estimated approximately in the following manner. According to Ostwald's dilution formula

$$\frac{\alpha_1}{v_1} = \frac{\alpha_2}{v_2},$$

when

$$\sqrt{k_1^2 + \frac{4k_1}{v_1}} - k_1 = \sqrt{k_2^2 + \frac{4k_2}{v_2}} - k_2.$$

[1] The subscript 1 always refers to acetic acid, while 2 refers to the cyanacetic acid.

[2] The word mol has come into general use indicating a gram-molecule.

Everything is known here except $v_1$ and $v_2$, and one of these can be expressed in terms of the other, thus :

$$1/76\ v_2 = 6.331 - 75/76\ v_1.$$

This value can then be substituted for $v_2$ in the preceding equation, and the equation solved for $v_1$. This would, however, be too complicated and tedious a process for practical use. Wakeman therefore finds by trial values for $v_1$ and $v_2$, which make

$$\frac{\alpha_1}{v_1} = \frac{\alpha_2}{v_2}.$$

When $v_1 = 3.0695$, and $v_2 = 250.93$, the solutions are isohydric, for from Ostwald's formula transformed,

$$\alpha = \tfrac{1}{2}\left[\sqrt{k^2v^2 + 4kv} - kv\right],$$

we obtain, by first substituting the value of $v_1$ and then of $v_2$ with the corresponding constant, $\alpha_1 = 0.007406$ and $\alpha_2 = 0.6053$, and we find

$$\frac{\alpha_1}{v_1} = \frac{\alpha_2}{v_2} = 0.002415.$$

In this mixture 75/76 mol acetic acid and 1/76 mol cyanacetic acid are present. The quantity of electricity, therefore, which is carried by the ions of the acetic acid is proportional to

$$75/76\ \alpha_1 = 75/76 \times 0.007406 = 0.007308,$$

and that carried by the ions of the cyanacetic acid is likewise proportional to

$$1/76\ \alpha_2 = 1/76 \times 0.6053 = 0.007965.$$

Hence the whole quantity of electricity carried by the solution is proportional to the sum of these two, or to 0.015273, and consequently this can be considered to be the degree of dissociation of a mol of the mixed acids at the dilution, $v = 6.331$.

Wakeman compared the values of $\alpha$ calculated in this way, at different dilutions with those derived directly from the conductivity of the mixture. The results are given in the accompanying table. The values of the Ostwald dissociation constant, as calculated from both values of $\alpha$, are shown in the last two columns.

CONDUCTIVITY OF MIXTURES OF ACETIC ACID AND CYANACETIC ACID IN THE RATIO OF 75 MOLS ACETIC ACID TO 1 MOL CYANACETIC ACID.

$k_1$ (acetic acid) = 0.000018. $k_2$ (cyanacetic acid) = 0.0037.

$\Lambda_\infty = 388$.

| v. | $\Lambda^1$. | $\frac{1000}{v}\alpha$. Measured. | $\frac{1000}{v}\alpha$. Calculated. | $\frac{1000}{v}k$. Measured. | $\frac{1000}{v}k$. Calculated. |
|---|---|---|---|---|---|
| 6.33 | 5.87 | 1.51 | 1.53 | 0.00367 | 0.00374 |
| 12.66 | 7.83 | 2.03 | 2.02 | 0.00327 | 0.00329 |
| 25.3 | 10.46 | 2.70 | 2.66 | 0.00295 | 0.00292 |
| 50.6 | 13.93 | 3.59 | 3.57 | 0.00264 | 0.00261 |
| 101.2 | 18.77 | 4.84 | 4.78 | 0.00243 | 0.00237 |
| 202.4 | 25.47 | 6.56 | 6.48 | 0.00228 | 0.00222 |
| 404.8 | 34.75 | 8.96 | 8.81 | 0.00218 | 0.00210 |
| 809.6 | 47.61 | 12.27 | 11.94 | 0.00212 | 0.00200 |

The values of $\alpha$ as calculated, agree excellently with those found from the measurement of the conductivity, which affords good evidence of the correctness of the theory of isohydric solutions. The small quantity of cyanacetic acid present is seen to exert considerable influence on the conductivity of the acetic acid, especially at the lower dilutions. This is shown by the fact that the dissociation constant is about twice as great as that of acetic acid alone at the earlier concentrations, but it rapidly decreases as the dilution increases until at the later dilution it does not differ much from that of acetic acid. Wakeman found that the effect of other acids on the conductivity of acetic acid was very similar to that just shown, the effect, of course, being less the weaker the acid and the more dilute its solution.

Quite recently Barmwater[2] has also treated this same subject from the standpoint of isohydrism. His results for the most part are similar to those obtained by Wakeman, his essential contribution being a new and more scientific method of approximation to determine the degree of dissociation of the electrolytes in a mixture.

**WOLF'S "D" VALUE.**—In general, when the component solutions of a mixture are not isohydric, the conductivity of the mixture is less than the mean of the conductivities of the component solutions. This is also expressed by saying that the conductivity of a mixture of electrolytes is usually less than the sum of the

[1] Wakeman expressed these results in mercury units. They have been recalculated to reciprocal ohms.

[2] *Ztschr. phys. Chem.*, 43, 557 (1903).

conductivities of the component electrolytes at the same concentration at which each exists in the mixture. Wolf[1] has investigated the conductivity of mixtures of dilute solutions of strong electrolytes with solutions of weak electrolytes, and he ascribes this decrease in conductivity just mentioned to three causes: *viz.*, to a decrease in the dissociation of the strong electrolyte by a change in the solvent caused by the presence of the weak electrolyte, to the retarding of the speed of the ions of the strong electrolyte on account of the increase in viscosity of the solvent due to the same cause, and finally to an isohydric influence depending on the double decomposition of the two electrolytes.

The second of these influences seems to be in general the more marked. It is well known that the addition of a small quantity of alcohol to a solution of an electrolyte increases the viscosity and at the same time decreases the conductivity. Wolf shows that the addition of a weak electrolyte like acetic acid has an effect very similar to that due to the addition of alcohol.[2] The following figures, taken from his results, will serve as an illustration.

FOURTH-NORMAL KCl + $n$ ALCOHOL.

| $n$. | $\kappa_1$. | $\kappa$ *found.* | $d$. | $D$. |
|---|---|---|---|---|
| 3.111 | 0.03052 | 0.01923 | 37.0 | 11.9 |
| 1.556 | 0.03052 | 0.02422 | 27.65 | 13.3 |
| 0.778 | 0.03052 | 0.02722 | 10.8 | 13.9 |
| 0.194 | 0.03052 | 0.02968 | 2.8 | 14.2 |

FOURTH-NORMAL KCl + $n$ ACETIC ACID.

| $n$. | $\kappa_1$. | $\kappa_2$. | $\kappa$ *calculated.* | $\kappa$ *found.* | $d$. | $D$. |
|---|---|---|---|---|---|---|
| 3.11 | 0.030572 | 0.001912 | 0.03248 | 0.02418 | 27.2 | 8.7 |
| 1.556 | 0.030572 | 0.001738 | 0.03231 | 0.02783 | 14.6 | 9.4 |
| 0.778 | 0.030572 | 0.001372 | 0.03194 | 0.02963 | 7.6 | 9.7 |
| 0.1945 | 0.030572 | 0.000731 | 0.03130 | 0.03071 | 1.9 | 9.95 |

$n$ Represents the concentration of the alcohol or acetic acid in normal terms, $\kappa_1$ is the conductivity of the potassium chloride solution as found $\kappa_2$ is the same for the acetic acid solution, $\kappa$ *found* is the conductivity of the mixture as found, $\kappa$ *cal* is the sum of $\kappa_1$ and $\kappa_2$, and $d$ and $D$ are obtained according to the following relations:

1 *Zischr. phys. Chem.*, 40, 222 (1902).

2 Arrhenius called attention to this fact some time ago: *Zischr. phys. Chem.*, 9, 506 (1892).

$$d = \frac{100\,\kappa\ cal. - \kappa\ found}{\kappa_1},$$

or in the first table,

$$= \frac{100(\kappa_1 - \kappa\ found)}{\kappa_1}, \text{ and } D = \frac{d}{n}.$$

$D$ is therefore the percentage depression of the conductivity of the potassium chloride solution produced by an addition of 1 gram-molecule of alcohol or of acetic acid. This is very nearly a constant in the two cases, which shows the effect of the addition of acetic acid is similar to that of the addition of alcohol, but less in degree. Wolf, therefore, considers the value of $D$ as an approximate measure of the increase in the viscosity of the solvent caused by the addition of another substance; he shows, however, that it is not directly proportional to this.

Rudorf[1] has investigated, at greater length, the relation between the $D$ value and the viscosity of the solution, and he has found that, although one can approximate to the effect of the viscosity from the value of $D$ in many cases, still no general relation can be established between them. He also finds the $D$ value less constant than Wolf did, the general rule being that it increases as the concentration of the solution increases until a maximum is reached, after which it decreases.

**DISSOCIATION OF ELECTROLYTES IN MIXTURES.**—When two electrolytes are present in the same solution, Schrader[2] has calculated the degree of dissociation of each in the following manner. Considering only primary separation at the electrodes, then

$$1 - n_1 = \frac{Z_1^a}{y_1^a},\ n_1 = \frac{Z_1^a}{y_1^a},$$

and

$$1 - n_2 = \frac{Z_2^a}{y_2^a},\ n_2 = \frac{Z_2^a}{y_2^a},$$

in which $n_1$ and $n_2$ are the transport numbers of the anions of the two electrolytes, $Z_1^a$ and $Z_2^a$ are the amounts of the anions that have migrated to the anode, $Z_1^c$ and $Z_2^c$ are the same for the cations, $y_1^a$ and $y_2^a$ are the amounts of the anions separated at the

[1] *Ztschr. phys. Chem.*, 43, 257 (1903).
[2] *Ztschr. Elektrochem.*, 3, 498 (1897).

electrodes, and $y_1'$ and $y_2'$ are the same for the cations. Dividing the first equation above by the third, and the second by the fourth, we obtain

$$\frac{y_1'}{y_2'} = \frac{Z_1'(1-n_2)}{Z_2'(1-n_1)} \text{ and } \frac{y_1''}{y_2''} = \frac{Z_1''n_2}{Z_2''n_1}. \qquad (1)$$

Now letting $i_1$ be the part of the current carried by electrolyte 1, and $i_2$ that carried by electrolyte 2, and letting further $A_1'$, $A_2''$, $A_1'$, $A_2'$ be the equivalent weights of the respective ions, then

$$y_1' = i_1A_1', \quad y_1'' = i_1A_1'',$$

and

$$y_2' = i_2A_2', \quad y_2'' = i_2A_2''.$$

If $x = \frac{i_1}{i_2}$, then

$$\frac{y_1'}{y_2'} = x\frac{A_1'}{A_2'}, \text{ and } \frac{y_1''}{y_2''} = x\frac{A_1''}{A_2''}. \qquad (2)$$

Combining (1) and (2) we have

$$x = \frac{Z_1''n_2A_2''}{Z_2''n_1A_1''} = \frac{Z_1'(1-n_2)A_2'}{Z_2'(1-n_1)A_1'}. \qquad (3)$$

We will let $\alpha_1'$ and $\alpha_2'$ represent the degree of dissociation of the two electrolytes in the mixture, and $l_{a_1}$ and $l_{c_1}$, and $l_{a_2}$ and $l_{c_2}$ be the migration numbers of the ions. Now since only the dissociated portion of the electrolytes take part, in carrying the current

$$\frac{y_1'}{A_1'} = \frac{y_1''}{A_1''} = m_1\alpha_1'(l_{a_1} + l_{c_1}), \text{ and } \frac{y_2'}{A_2'} = \frac{y_2''}{A_2''} = m_2\alpha_2'(l_{a_2} + l_{c_2}), \quad (4),$$

in which $\frac{y_1'}{A_1'}$, etc. represent the amount of each ion separated at the electrodes in terms of equivalents, and $m_1$ and $m_2$ are the concentrations of the two electrolytes. From equations (2) and (4) we obtain

$$x = \frac{m_1\alpha_1'(l_{a_1} + l_{c_1})}{m_2\alpha_2'(l_{a_2} + l_{c_2})}.$$

Since $l_{a_1} + l_{c_1} = \Lambda_{\infty_1}$ and $l_{a_2} + l_{c_2} = \Lambda_{\infty_2}$,

$$x = \frac{m_1\alpha_1'\Lambda_{\infty_1}}{m_2\alpha_2'\Lambda_{\infty_2}}. \qquad (5)$$

For the single electrolytes let $\alpha_1$ and $\alpha_2$ be the degree of dissociation, $\kappa_1$ and $\kappa_2$ be the specific conductivity and $\Lambda_1$ and $\Lambda_2$ be

the equivalent conductivity of each respectively. From the equation of Arrhenius (page 51) we have

$$\frac{\alpha_1}{\alpha_2} = \frac{\Lambda_1 \Lambda_{\infty_2}}{\Lambda_2 \Lambda_{\infty_1}}.$$

Since $\Lambda_1 = \frac{1000\kappa_1}{m_1}$ and $\Lambda_2 = \frac{1000\kappa_2}{m_2}$, we have, combining the last equation with (5),

$$\frac{\alpha_1'}{\alpha_2'} = \frac{\alpha_1}{\alpha_2} x \frac{\kappa_2}{\kappa_1}.$$

There will therefore be no change in the degree of dissociation of the electrolytes when mixed, if $x = \frac{\kappa_1}{\kappa_2}$. But if $x \gtrless \frac{\kappa_1}{\kappa_2}$, then $\frac{\alpha_1'}{\alpha_2'} \gtrless \frac{\alpha_1}{\alpha_2}$. The accompanying table gives the value of these quantities for solutions of KI and KCl. The subscript 1 indicates the former electrolyte.

| Solution No. | Concentration of KI ($m_1$). | Concentration of KCl ($m_2$). | $m_1/m_2$. | $x$. | $\kappa_1/\kappa_2$. |
|---|---|---|---|---|---|
| 1 | 0.02595 | 0.02571 | 1.009 | 0.997 | 1.027 |
| 2 | 0.03442 | 0.04748 | 0.725 | 0.704 | 0.751 |
| 3 | 0.03074 | 0.06176 | 0.498 | 0.500 | 0.522 |
| 4 | 0.01992 | 0.03720 | 0.535 | 0.486 | 0.557 |

In this case, therefore, $x < \frac{\kappa_1}{\kappa_2}$, and consequently $\frac{\alpha_1'}{\alpha_2'} < \frac{\alpha_1}{\alpha_2}$.

To find the value of $\alpha_1'$ and $\alpha_2'$ we can consider that no contraction of volume takes place on mixing the solutions of the single electrolytes and that, therefore, the specific conductivity of the mixture is

$$\kappa = \frac{m_1}{1000} \alpha_1' \Lambda_{\infty 1} + \frac{m_2}{1000} \alpha_2' \Lambda_{\infty 2}.$$

Combining this with (5) we have

$$\alpha_1' = \frac{1000\kappa x}{m_1 \Lambda_{\infty 1}(x+1)}, \text{ and } \alpha_2' = \frac{1000\kappa}{m_2 \Lambda_{\infty 2}(x+1)}.$$

The values of $\alpha_1'$ and $\alpha_2'$ calculated according to these formulas for the mixtures of KI and KCl, whose concentrations were given in the preceding table, are shown below. The degrees of dissociation of the single electrolytes at the same concentrations are given for comparison.

| Solution No. | $\alpha_1'$. | $\alpha_2'$. | $\alpha_1$. | $\alpha_2$. |
|---|---|---|---|---|
| 1 | 0.843 | 0.854 | 0.903 | 0.888 |
| 2 | 0.852 | 0.877 | 0.891 | 0.860 |
| 3 | 0.847 | 0.843 | 0.896 | 0.854 |
| 4 | 0.806 | 0.886 | 0.911 | 0.874 |

The change in dissociation on mixing is not very great for these electrolytes. Schrader also calculated the degree of dissociation of $H_2SO_4$ and $CuSO_4$ in mixtures of each other, and found that the dissociation of the former was decreased and that of the latter was increased very considerably by mixing.

Hoffmeister[1] has calculated the concentration of the cations in a mixture of two binary electrolytes, having a common anion by means of an equation derived by Jahn, *viz.*

$$C = 1.0784 \frac{ak}{Acu} . 10^{-9};^{2}$$

$a$ is the amount of the cation which has migrated from the anode during the time that $c$ grams of silver have been deposited in the voltameter, $A$ is the equivalent weight of the cation and $u$ its migration number, and $k$ is the specific conductivity of the mixture. He employed mixtures of $AgNO_3$ and $HNO_3$, and of $NaC_2H_3O_2$ and $HC_2H_3O_2$. In the former case the dissociation of the electrolyte present in excess was not much influenced by the presence of the other, while the dissociation of the one whose concentration was less was considerably decreased. In the latter case the acetic acid exercised no perceptible influence on the dissociation of the sodium acetate.

Hopfgartner[3] has found the ratio of the concentrations of the cations in a mixture of two electrolytes from a determination of their transport numbers in the given condition. The theoretical considerations involved are as follows:

Let $c_1$ and $c_2$ be the concentrations of the cations, and $a_1$ and $a_2$ the quantity of each which passes a cross section of the apparatus

[1] *Zischr. phys. Chem.*, 27, 345 (1898).

[2] This formula is expressed in terms of mercury units; in terms of the Kohlrausch units it becomes,

$$C = 107.93 \frac{ak}{Acl}.$$

[3] *Zischr. phys. Chem.*, 25, 115 (1898).

in the unit of time, and $U_1$ and $U_2$ their absolute speeds, we then have

$$a_1 = c_1 U_1, \text{ and } a_2 = c_2 U_2.$$

But $U = l \varepsilon E$, therefore

$$a_1 = c_1 l_{c_1} \varepsilon E, \text{ and } a_2 = c_2 l_{c_2} \varepsilon E,$$

in which $l_{c_1}$ and $l_{c_2}$ are the migration numbers of the cations, $\varepsilon$ is the charge on each gram-ion and $E$ is the potential difference between the electrodes. Dividing one of these by the other,

$$\frac{a_1}{a_2} = \frac{c_1 l_{c_1}}{c_2 l_{c_2}}, \text{ or } \frac{c_1}{c_2} = \frac{a_1 l_{c_2}}{a_2 l_{c_1}}.$$

Since $\frac{l_{c_2}}{l_{c_1}}$ is practically constant, the last equation signifies that the ratio of the concentrations of two cations is proportional to the quantities of these ions carried by the current to the cathode.

Hopfgartner tested this by determining the decrease at the anode in the concentrations of the cations of two mixed electrolytes having a common anion, and thereby finding values for $a_1$ and $a_2$. His results show that the ratio of the concentrations of the cations in a mixture of two well dissociated binary electrolytes is not very different from the ratio of their concentrations when the electrolytes are in solution singly. When, however, one of the electrolytes is bivalent, as $BaCl_2$, the difference is quite considerable, possibly because the dissociation of such electrolytes is not so simple as was assumed.

The derivation of Schrader's results (page 110) was based on the hypothesis that, considering only primary separation at the electrodes,

$$1 - n_1 = \frac{Z_1^c}{y_1^c}, \text{ and } 1 - n_2 = \frac{Z_2^c}{y_2^c},$$

that is, that the transport numbers of electrolytes remain unchanged in mixtures. By transformation

$$y_1^c = \frac{Z_1^c}{1 - n_1}, \text{ and } y_2^c = \frac{Z_2^c}{1 - n^2},$$

from which, if $n$ is known for the single electrolytes, the amounts of each cation separated at the electrode can be calculated. Then, if the hypothesis is correct, the sum of the amounts of silver

equivalent to these should be equal to the amount of silver deposited in the voltameter. Hopfgartner applied the data he had collected to an investigation of this point. Most of his results are shown in the accompanying table.

| Separated at cathode. No. | H. | Silver calculated from these. | Silver in voltameter. | Difference in per cent. of silver found. |
|---|---|---|---|---|
| | 1 vol. N/1-NaCl + 9 vol. N/1-HCl. | | | |
| 0.0155 | 0.02074 | 2.3042 | 2.3475 | —1.8 |
| 0.0149 | 0.01662 | 1.8576 | 1.897 | —2.1 |
| | 1 vol. N/1-NaCl + 4 vol. N/1-HCl. | | | |
| 0.02646 | 0.01889 | 2.1562 | 2.195 | —1.8 |
| 0.0246 | 0.01326 | 1.5417 | 1.559 | —1.1 |
| 0.0254 | 0.01609 | 1.8500 | 1.820 | +1.7 |
| | 4 vol. N/1-NaCl + 1 vol. N/1-HCl. | | | |
| 0.1257 | 0.00467 | 1.0902 | 1.121 | —2.8 |
| 0.2211 | 0.007170 | 1.8052 | 1.743 | +3.6 |
| 0.2167 | 0.007999 | 1.8739 | 1.845 | +1.6 |
| | 9 vol. N/1-NaCl + 1 vol. N/1-HCl. | | | |
| 0.2274 | 0.0004321 | 1.5281 | 1.545 | —1.2 |
| 0.2156 | 0.000461 | 1.5062 | 1.545 | —2.5 |
| | 1 vol. N/5-NaCl + 1 vol. N/5-HCl. | | | |
| 0.0285 | 0.005255 | 0.6987 | 0.716 | —2.4 |
| 0.0690 | 0.009525 | 1.3478 | 1.360 | —0.9 |
| 0.0768 | 0.01089 | 1.5291 | 1.561 | —2.0 |
| Separated at cathode. Ba. | H. | Silver calculated from these. | Silver in voltameter. | Difference in per cent. of silver found. |
| | 1 vol. N/1-$BaCl_2$ + 4 vol. N/1-HCl. | | | |
| 0.0814 | 0.02213 | 2.5093 | 2.562 | —2.0 |
| 0.1056 | 0.02209 | 2.5432 | 2.562 | —0.7 |
| 0.0147 | 0.00835 | 0.9216 | 0.938 | —1.7 |
| | 1 vol. N/1-$BaCl_2$ + 1 vol. N/1-HCl. | | | |
| 0.238 | 0.01527 | 2.0179 | 2.075 | —2.7 |
| 0.1625 | 0.01178 | 1.5235 | 1.591 | —4.2 |
| 0.1373 | 0.010455 | 1.3412 | 1.405 | —4.5 |
| | 1 vol. N/5-$BaCl_2$ + 1 vol. N/5-HCl. | | | |
| 0.1716 | 0.009750 | 1.3193 | 1.320 | —0.05 |
| 0.1517 | 0.009855 | 1.2993 | 1.320 | —1.6 |
| 0.0370 | 0.00372 | 0.4585 | 0.470 | —2.6 |

The agreement in these tables between the amount of silver found and that calculated is good, when it is considered that the

amount calculated depends on the determination of two sets of transport numbers, one for the single electrolytes and one for the mixtures. The transport numbers of electrolytes, therefore, seem to be uninfluenced by mixing even at higher concentrations than those at which Schrader worked.

**DOUBLE SALTS.**—Some time ago Bender[1] and Klein[2] found that the conductivity of solutions of mixtures of two salts possessing a common ion is somewhat less than the sum of the conductivities of the two salts separately, but that when the two salts were capable of forming a double salt the conductivity was found to be very much less than the sum of the conductivities of the constituents. Quite recently Jones and his students[3] have made a number of investigations along this line.

Their results, which confirm, in general, the conclusions reached by Bender and by Klein, may be summed up as follows: (1) Mixtures of electrolytes not capable of forming double salts possess a conductivity which is always somewhat less than the sum of the conductivities of the electrolytes separately. (2) Experiments with a variety of types of double salts, as, for instance, double sulphates, chlorides, bromides, iodides, cyanides and nitrates, showed that the conductivity of such double salts is always less than the conductivities of the constituents separately, that this difference decreases as the concentration decreases, that this difference is greater than when the two substances are not able to form a double salt, and that it persists at greater dilutions. (3) The conductivity of a double salt is somewhat less than the conductivity of a mixture of its own components. This apparently shows that the state of equilibrium is different when a double salt is dissolved in water from that when its constituents are mixed together in water.

Rosenheim and Bertheim[4] have recently investigated the conductivity of mixtures of different acids for the purpose of ascertaining whether they form double compounds. They found that

[1] *Wied. Ann.*, 22, 179 (1884).

[2] *Ibid.*, 27, 151 (1886).

[3] Jones and Mackay : *Am. Chem. J.*, 19, 83 (1897) ; Jones and Ota : *Ibid.*, 22, 5 (1899) ; Jones and Knight : *Ibid.*, 22, 110 ; Jones and Caldwell : *Ibid.*, 25, 349 (1901) ; see also Lindsay : *Ibid.*, 25, 62.

[4] *Ztschr. anorg. Chem.*, 34, 427 (1903) ; see also in this connection, Hofmann: *Ztschr. phys. Chem.*, 45, 584 (1903).

the conductivity of a mixture of tartaric and malic acids is considerably greater than the sum of the conductivities of each singly. They, therefore, inferred that if the conductivity of a mixture of two acids is either much greater or much less than the sum of the conductivities of the single acids, the formation of a double compound is indicated. They then employed this method to investigate mixtures of phosphoric and molybdic acids, and found evidence for the existence of at least one and perhaps more compounds between them.

## CHAPTER XI.

### Applications of Conductivity Measurements.

**DETERMINATION OF THE BASICITY OF ACIDS.**—Ostwald[1] has devised an empirical method for determining the basicity of an acid from the conductivity of its normal sodium salt. An examination of the table (page 84) shows that the difference in the conductivity of a sodium salt of a dibasic acid, as $Na_2SO_4$, at successive dilutions is about twice as great as the corresponding difference in that of a sodium salt of a monobasic acid, as NaCl. For the sodium salt of a tribasic acid this difference would be about three times as great as that for the sodium salt of a monobasic acid, and so on.

The difference between the equivalent conductivity at $v = 32$ and that at $v = 1024$ is for the sodium salts of monobasic acids approximately equal to 10 at 25°. Ostwald's rule is, therefore, to find $\Delta$, the difference between the equivalent conductivities at 25° of the sodium salt of the acid at $v = 32$ and at $v = 1024$, then $n$, the basicity of the acid, will be equal to $\frac{\Delta}{10}$. This has been found to hold fairly well for those acids with which it has been tried and whose basicity runs from 1 up as high as 5.

The solution of the sodium salt may be obtained from the solution of the acid to be investigated by neutralizing a suitable quantity of this solution with a sixteenth-normal solution of pure sodium hydroxide, using a drop of phenolphthalein as indicator The resulting solution is then diluted so that the concentration of the salt will be thirty-second-normal. If the acid is insoluble in water some of it may be added directly to a given volume of the sodium hydroxide solution until the color of the indicator just disappears. After filtering, the solution is neutralized exactly, if necessary, by means of a drop or two of sodium hydroxide solution. The solution, however, should not react alkaline. The 1024th-normal solution can be readily obtained from the thirty-second-normal by dilution.

[1] *Ztschr. phys. Chem.*, 1, 105 (1887), and 2, 901 (1888); see also Ostwald and Luther: *Physico-chemische Messungen*, p. 423.

The accompanying results were obtained by Ostwald with sodium pyridinetricarbonate at 25°. Under $\mu$ the conductivity is given in reciprocal mercury units, which were used by Ostwald

| $v$. | $\mu$. | $\Lambda$. |
|---|---|---|
| 32 | 82.1 | 87.5 |
| 1024 | 113.1 | 120.6 |
| | $\Delta = 31.0$ | 33.1 |

in these measurements. Under $\Lambda$ the same is expressed in reciprocal ohms. Applying the formula, $n = \frac{\Delta}{10}$, we have $n = 3.1$ from $\mu$ and 3.3 from $\Lambda$. The basicity is thus found to be 3. Since, however, the formula was derived with conductivities expressed in the old units, and furthermore, since the units now in use are 1.063 times smaller than the old (in Ostwald's work, 1.066), the rule is better expressed, when conductivities are given in reciprocal ohms, by $n = \frac{\Delta}{11}$.

**TITRATION OF ACIDS AND BASES BY MEASURING CONDUCTIVITY.**—On account of the rapid rate of migration of H and OH ions, solutions of acids and of bases possess a greater specific conductivity than solutions of neutral salts of the same concentration. Advantage can be taken of this fact to determine the neutral point when neutralizing a base with an acid, or *vice versa*. When near the neutral point the conductivity is measured after each successive addition of a small quantity of the acid or of the base. The solution is neutral when the conductivity is a minimum. Plotting the results in a curve (see Chapter VIII) aids greatly in fixing the minimum.

This method is, of course, slow and is consequently only of value where indicators cannot safely be employed. It, moreover, cannot be used when the salt formed undergoes hydrolytic decomposition.[1]

**DETERMINATION OF THE PURITY OF LIQUIDS.**—As was shown in the chapter on the conductivity of water (Chapter V), the specific conductivity of a sample of this liquid supplies a simple and sure means of judging its purity. The purity of other

[1] For a more complete exposition of the method, see Kohlrausch: *Ztschr. phys. Chem.*, 12, 773 (1893); 33, 257 (1900); also Dülliberg, *Ibid.*, 45, 137 (1903).

liquids can be estimated in precisely the same manner. However, the conductivity of but few liquids has been investigated as thoroughly as that of water, so that the data for the estimation of the degree of impurity of most of them are very incomplete. Sufficient determinations of the conductivity of non-aqueous liquids have been made (see appendix, Table 9) to illustrate the usefulness of the method. Some of the values of the conductivity of methyl alcohol, which have been found at 25°, are given below.

SPECIFIC CONDUCTIVITY OF METHYL ALCOHOL.

| Authority. | $\kappa \times 10^6$. |
|---|---|
| Carrara | 0.072 |
| Walden | 1.45 |
| Schall | 1 to 2 |
| Jones and Lindsay | 2.3 |
| Carrara and Levi | 2.5 |
| Kahlenberg and Lincoln | 5.7 |
| Zelinsky and Krapiwin | 18 to 30 |

Carrara obtained the low value, given above, by distilling *in vacuo* a product which had been purified as completely as possible by other means. Without the conductivity method it would very likely be extremely difficult to estimate the difference in purity of the above samples, and no other method, to say the least, could be applied with equal rapidity.

Walden has recently made a wide application of this method in determining the purity of a number of organic solvents. His results with acetonitrile[1] are given as an example.

The sample employed was a preparation of Merck. It was first shaken up with lead oxide and then distilled from phosphorus pentoxide, passing over between 80° and 80.5°, from which it was inferred to be practically pure. The conductivity showed this, however, to be far from the case.

| | $\kappa \times 10^6$. |
|---|---|
| Fraction from 1st distillation from $P_2O_5$ | 4.45 |
| " " 2nd " " " | 3.0 |
| " " 3rd " " " | 1.3 |
| " " 4th " " " | 2.06 |

Stood 3 years in a brown bottle, and then distilled from $Na_2SO_4$:

| | |
|---|---|
| Fraction from 1st distillate | 1.8 |
| " " 2nd " | 0.6 |

[1] *Zischr. phys. Chem.*, 46, 149–151 (1903).

Stood a month over $P_2O_5$ with frequent shaking and then distilled :

| | |
|---|---|
| Fraction from 1st distillate | 0.41 |
| " " 2nd " | 0.396 |

This last value was the lowest obtained and is somewhat less than one-tenth that given by the first distillate from $P_2O_5$, which was considered to be a practically pure sample.

**DETERMINATION OF THE POINT OF SOLIDIFICATION OF FUSED SALTS.**—As is pointed out in the latter part of the next chapter, fused salts conduct electricity quite well, and solid salts, near their fusing point, also possess some conductivity, although considerably less than when melted. Liebknecht and Nilsen[1] have recently developed a method for determining the solidifying point or fusing point of an electrolyte based on these facts.

They employed a three-limbed tube of hard glass as conductivity vessel. The outside limbs served for the insertion of the electrodes, while the middle one held a thermometer, or at high temperature a thermocouple. The substance under investigation was melted in the tube; then, as it was slowly cooled, the conductivity was measured by the Kohlrausch method with telephone and alternating current, the temperature being taken at the time of each measurement. On plotting the conductivities thus obtained the point of solidification would be indicated by a sudden change in the direction of the curve. By starting with the solid substance, just below its melting-point, this point could be determined in the same manner by gradually raising the temperature. A sharper minimum was obtainable with the telephone by using carbon electrodes than by using metallic ones. The solidifying point of mixtures was also investigated, and it was found that this point was identical for such pairs of salts as KCl and NaF, and NaCl and KF.

**ANALYSIS OF SOLUTIONS CONTAINING A SINGLE ELECTROLYTE.**—Since the conductivity of nearly all electrolytes is a simple function of their concentration, if a solution is known to contain a certain substance in the pure state, the concentration can be found by measuring the conductivity. For this purpose tables of the conductivity of electrolytes are indispensable. Many such

[1] *Berichte*, 36, 3718 (1903).

tables will be found in the appendix of this book. A more complete set is given by Kohlrausch and Holborn, *Leitvermögen der Elektrolyte.*

From tables which give specific conductivities the concentration can be at once found by interpolation from the determined value of the specific conductivity of the solution. If it is necessary to use a table in which the equivalent conductivity alone is given, a small table of specific conductivities for the range required should be calculated from it. In most cases interpolation will be easier and more accurate when made from a curve constructed from the given specific conductivities (Chapter VIII). In case the temperature at which the conductivity measurements are made is not the same as that for which the values in the table are given, the measurements should be reduced by the proper temperature coefficients.

When the solution is concentrated difficulties are sometimes encountered in estimating the concentration on account of the conductivity being in the vicinity of its maximum value. In such cases the solution should be diluted with from two to four volumes of water, according to the nature of the substance, before the conductivity is determined. When the solution is very dilute, more difficulty is experienced in accurately determining the concentration from the conductivity on account of the influence of the conductivity of the water employed. In case the substance in solution is a neutral salt, a fairly accurate value will be obtained by simply substracting the conductivity of the water from that of the solution.

Van't Hoff[1] has found a method similar to this useful in determining when water is completely saturated with a mixture of salts. When employed in connection with the specific gravity he was able to determine, for instance, when a solution was saturated with a mixture of sodium chloride, magnesium chloride and carnallite. The agitation of the solution is continued until the conductivity becomes constant. With proper precautions the method is very helpful, particularly in cases where the density of the solution changes but little as the point of saturation is approached.

[1] *Ztschr. Elektrochem.*, 6, 57 (1899). See also Dawson and Williams, *Ibid.*, 6, 141 (1899)

**DETERMINATION OF THE SOLUBILITY OF DIFFICULTLY SOLUBLE SALTS.**—The principle in this case is the same as in the analysis of a dilute solution containing a single electrolyte, except that for the majority of difficultly soluble salts no conductivity tables are at hand from which interpolations can be made. Approximate values of the conductivity of such salts can, however, be calculated from the migration numbers of the different ions (pages 73, 78) and from the differences between $\Lambda_\infty$ and $\Lambda_v$ at different concentrations, as given on page 84, as will be illustrated below.

The water used in determinations of this kind should be of a high degree of purity, and its specific conductivity must be known. The substance whose solubility is to be determined is pulverized in an agate mortar, and the powder so obtained is repeatedly shaken up with water, each time the turbid liquid being carefully decanted or siphoned off from the material which has settled. Finally, when the residue has largely subsided after the last treatment with water, a portion of the still slightly turbid liquid is removed with a pipette to a conductivity cell of one of the forms shown in Fig. 5, and the conductivity measured. The substance is again shaken up with water, and the conductivity redetermined until it is found to be constant. If a gradual uniform change is observed in the conductivity, it may be due to decomposition of the substance or to a change in the amount of water of crystallization, both of which affect the degree of solubility.

When the greatest accuracy is desired the final saturation should be conducted directly in the conductivity vessel, which must then be of a suitable form. Kohlrausch[1] has used a form similar to that shown in Fig. 5, *b*, into which a thermometer projects. Saturation is accomplished by rapidly rotating the vessel, the conductivity being measured from time to time until it becomes constant. The time required for saturation varies greatly for different substances. For illustrations of different behavior in this respect consult the paper of Kohlrausch just cited.

Having determined the conductivity of the saturated solution in either of the above ways, the conductivity of the water used in preparing the solution is subtracted, and from the difference, $\kappa$,

[1] *Zeschr. phys. Chem.*, 44, 197 (1903).

the concentration of the solution is estimated. A few examples will best illustrate the method of calculation.

(1) Silver Chloride at 18°. Conductivity of water $= 1.25 \times 10^{-6}$. Conductivity of saturated solution $= 2.48 \times 10^{-6}$, therefore $\kappa = 1.23 \times 10^{-6}$ for AgCl alone. From $l_a + l_c$, (Table, page 73) $\Lambda_\infty$ for AgCl $= 119.6$. By means of the numbers in column $d_1$, page 84, the following values of the conductivity may be calculated from $\Lambda_\infty$.

| $m = 1000\eta$. | $\Lambda$. | $\kappa = \eta\Lambda$. |
|---|---|---|
| 0.0001 | 118.6 | $11.86 \times 10^{-6}$ |
| 0.0001 | 118.8 | $63.64 \times 10^{-6}$ |

To obtain an approximate value of the concentration when $\kappa = 1.23 \times 10^{-6}$, we have

$$1000\eta = \frac{1.23}{11.86} \times 0.0001 = 0.00001037.$$

A value more nearly accurate is found from the equivalent conductivity, because this varies but little with the concentration. The interpolated value of $\Lambda$ from the concentration already found, is 119.4. From this the concentration is found as follows:

$$\eta = \frac{\kappa}{\Lambda} = \frac{1.23 \times 10^{-6}}{119.4} = 0.0103 \times 10^{-6}.$$

The concentration is, therefore, $0.0103 \times 10^{-6}$ gram-equivalent per cubic centimeter, or 0.0103 milligram-equivalent per liter. Multiplying this by the equivalent weight, which in this case is also the molecular weight, 143.4, the concentration is found to be 1.48 mg. per liter.

(2) Barium oxalate (anhydrous) at 18°. Conductivity of water $= 1.3 \times 10^{-6}$. Conductivity of saturated solution $= 71.7 \times 10^{-6}$. $\kappa = 70.4 \times 10^{-6}$ for $\frac{1}{2}BaC_2O_4$ alone. From table, page 78, $\Lambda_\infty = 119$. From this and from the numbers in column $d_2$, page 84, we can construct the following table:

| $m = 1000\eta$. | $\Lambda$. | $\kappa = \eta\Lambda$. |
|---|---|---|
| 0.0001 | 114 | $11.4 \times 10^{-6}$ |
| 0.0002 | 112 | $22.4 \times 10^{-6}$ |
| 0.0005 | 108 | $54.0 \times 10^{-6}$ |
| 0.001 | 103 | $103.0 \times 10^{-6}$ |

The approximate value of the concentration is, therefore,

$$1000\eta = 0.0005 + \frac{16.4}{49} \times 0.0005 = 0.000667.$$

Interpolating to find the equivalent conductivity at this concentration, we obtain as its approximate value 106. From this the more accurate value of the concentration is obtained:

$$\eta = \frac{\kappa}{\Lambda} = \frac{70.4 \times 10^{-6}}{106} = 0.66 \times 10^{-4} \text{ gram-equiv. per cc.}$$

Multiplying by the equivalent weight, 112.5, the concentration of a saturated solution of barium oxalate at 18° is found to be 74.3 mg. per liter.

Kohlrausch[1] and also Böttger[2] have recently determined, with the greatest care, the conductivity of many difficultly soluble salts (see appendix, Tables 7 and 8). The latter has also calculated the solubilities of the salts investigated.

**ANALYSIS OF MIXTURES CONTAINING TWO ELECTROLYTES.**—Sufficient data are not yet at hand to determine, in general, by means of conductivity measurements the quantities of two electrolytes present in a solution. For such to be possible, another property must also be known besides the conductivity, as, for instance, the specific gravity or the index of refraction. Furthermore, tables would be required connecting these different properties with the concentration of the solution and with the relative quantities of the two substances.

The conductivity may, however, be of service in many cases in fixing the relative quantities of two electrolytes in a solid mixture. In general, the following method, suggested by Kohlrausch, might be employed in such a case. The mixture is dissolved in water to a definite concentration, for example, 5 per cent., and the conductivity of the resulting solution measured. Then by determining the conductivity of solutions formed by dissolving different relative proportions of the same substances so that the total concentration will be the same, *viz.*, 5 per cent., a table could be constructed from which the unknown ratio in which the substances exist in the mixture could be estimated. Such a method is, however, so laborious that it will hardly come into general use, except where there is constant need of determining the concentration of solutions containing always the same two substances.

[1] *Ztschr. phys. Chem.*, 44, 197 (1903).

[2] *Ibid.*, 46, 521 (1903). The method of calculating the solubility is considered in detail in this article.

There are certain cases, however, where the conductivity of the mixture is the mean of the conductivities of the two components, in which this method may be quite useful. It has been shown at the beginning of this chapter that the above conditions hold only when the solutions of the single substances are isohydric, that is, have a common ion of the same concentration in each. This is practically true also for salts of a similar nature at the same concentration, as, for example, the chlorides, bromides and iodides of the same metal, or the same salts of allied metals. In such cases it can be assumed that the conductivity of the mixture is the mean of the conductivities of the components, when the solutions of the components are of equal concentration. This means that if the conductivities of solutions of KCl and KBr of equal concentration are $\kappa_1$ and $\kappa_2$ and that of any mixture of these two solutions containing $A$ parts of the former substance and $B$ parts of the latter is $\kappa$, then

$$\kappa = \frac{\kappa_1 A + \kappa_2 B}{A + B}$$

If we consider, for the sake of simplicity, that $A$ and $B$ are the quantities of the two substances in a unit quantity of the solid mixture, that is, $A + B = 1$, it follows that

$$\kappa = A\kappa_1 + (1 - A)\kappa_2.$$

When $\kappa_2$ is greater than $\kappa_1$,

$$A = \frac{\kappa_2 - \kappa}{\kappa_2 - \kappa_1}, \quad B = \frac{\kappa - \kappa}{\kappa_2 - \kappa_1} \text{ and } \frac{A}{B} = \frac{\kappa_2 - \kappa}{\kappa - \kappa_1},$$

which shows that only the ratio of the conductivities are required in order to calculate $A$ or $B$. If, therefore, the same resistance is retained at $R$ in the Wheatstone bridge arrangement (Chapter I, Fig. 3) while the different conductivities are being measured, the ratio, as taken directly from Obach's table, can be employed in each case instead of the actual conductivity.[1]

The following example, with a mixture containing KCl and KBr, will illustrate the method: $a$ is the position on the bridge and $\kappa$ the corresponding number from Obach's table for a 5 per cent. solution of the mixture, $a_1$, $a_2$ and $\kappa_1$, $\kappa_2$ the similar quantities for 5 per cent. solutions of the pure components.

[1] For further discussion of this method see Erdmann: *Berichte*, 30, 1175 (1897).

| Unknown mixture. | KCl. | KBr. |
|---|---|---|
| $a = 498.0$ | $a_2 = 701.3$ | $a_1 = 475.5$ |
| $\kappa = 0.9920$ | $\kappa_2 = 2.348$ | $\kappa_1 = 0.9066$ |

$$B = \frac{\kappa - \kappa_1}{\kappa_2 - \kappa_1} = \frac{0.9920 - 0.9066}{2.348 - 0.9066} = \frac{0.0854}{1.4414} = 0.0592.$$

Therefore, KCl is found to compose 5.92 per cent. of the mixture.

## CHAPTER XII.

### Conductivity of Single Substances.

**INTRODUCTION.**—Heretofore we have discussed almost exclusively the conductivity of aqueous solutions, that is, of mixtures of the so-called electrolytes with water. These are the best conducting liquid media. Incidentally, the conductivity of water has been considered. We shall now pass to a consideration of the conductivity of single substances, which is quite analogous to the conductivity of water itself.

First, the conductivity of those substances which are either liquid at ordinary temperatures or can be liquefied by means of pressure at slightly lower temperatures will be taken up. Then we shall discuss the conductivity of substances which are solid at ordinary temperatures, but possess a conductivity after they have been converted into the liquid state by fusion. Thirdly, attention will be called to the conductivity of certain solid compounds which retain their conductivity even below the fusing point. This last subject does not strictly belong in a book on the conductivity of liquids, but, since it is closely related to the conductivity of fused solids, mention will be made of it in this connection.

**METHODS EMPLOYED IN MEASURING THE CONDUCTIVITY OF OF PURE LIQUIDS.**—Within recent years the conductivity of a considerable number of non-aqueous liquids has been measured, chiefly in connection with investigations on the conductivity of non-aqueous solutions in which these liquids were used as solvents.

In nearly every instance the method of Kohlrausch with Wheatstone bridge and alternating current has been used. Wildermann[1] has, however, successfully employed another method. He used a direct current with great external resistance and measured the current strength with a galvanometer. The only advantage he claims for it over the Kohlrausch method is that he considers it yields more accurate results when measuring the conductivity of liquids possessing enormous resistances.

[1] *Ztschr. phys. Chem.*, 14, 247 (1894).

Since the resistances of the liquids are, in most cases, very great, special attention should be given to the compensating resistances which must occasionally be as high as 400,000 ohms. It is impossible to use the ordinary kind of differentially wound resistance coils for this purpose on account of their capacity. Graphite lines on glass have been used by some investigators for resistances over 1000 ohms.[1] These resistances, however, exhibit considerable fluctuation from time to time, so that unless frequently controlled their value is uncertain. Wildermann succeeded in preparing resistances of this kind which remained constant long enough to make a series of measurements (see page 18). Cohen[2] used resistance coils made by winding a single wire alternately forwards and backwards, according to the method of Chaperon. By such winding, capacity is largely eliminated, while the resistances are still free from induction. When measuring very high resistances, it is advisable to use a condenser to compensate the capacity of the resistance coils. No difficulty then is commonly experienced in obtaining a sharp minimum with the telephone.

Electrolytic vessels employed for non-aqueous liquids are usually similar to those used in determining the conductivity of water and should have a small resistance capacity. Any of the forms of vessel shown in Figs. 5 and 6 (Chapter II) are suitable for this purpose. The one devised by Arrhenius is probably more frequently employed than any other. When, however, the conductivity of a liquid possessing enormous resistance is to be measured the forms shown in Fig. 6 are preferable. Special types of vessel are used in many instances, particularly where from the nature of the liquid it is necessary to subject it to unusual temperatures or pressures.[3]

Nearly all investigators in this field have used electrodes covered with platinum black, for the reason that the readings are less liable to fluctuation than when blank electrodes are used. It is necessary, however, in the case of most organic liquids to avoid prolonged contact with platinized electrodes on account of in-

[1] Völlmer: *Wied. Ann.*, **52**, 328 (1894); Wildermann: *Zischr. phys. Chem.* **14**, 231 (1894).
[2] *Zischr. phys. Chem.*, **28**, 17 (1898).
[3] See Goodwin and Thompson: *Phys. Rev.*, **8**, 38 (1899); Walden and Centnerszwer: *Zischr. phys. Chem.*, **39**, 517 (1902).

cipient oxidation. Cohen[1] found that at 25°, when alcohol is used, this oxidizing action is so great as to preclude accurate measurement, but at 18° it is slow enough not appreciably to affect the readings when proper precautions are taken. Some investgators, as, for instance, Euler[2] and Walden,[3] have used blank electrodes successfully.

**VALUES OF THE CONDUCTIVITY OF PURE LIQUIDS.**—The conductivity of most pure liquids is slight, being of about the same order as the conductivity of pure water. The values of the conductivity of such liquids, both organic and inorganic, are given in the appendix, Table 9. An inspection of this table shows that values of the conductivity of the same substance as found by different investigators vary in many instances quite considerably. This is undoubtedly due to different degrees of purity of the liquids employed. A comparison of the values found by Frenzel and by Franklin and Kraus for the conductivity of ammonia, and by Carrara for the conductivity of methyl alcohol, with the values obtained by others, serves to show how much conductivity is reduced by efficient purification. The same may be said of many of Walden's results. Most of the values, therefore, in the table are to be looked upon simply as upper limits, the true conductivity of the pure substance being very likely somewhat lower. If subjected to rigorous methods of purification, the fatty acids, with the exception of formic acid, would probably be found to be non-conductors. Examples of the effect of such purification are considered more at length in the preceding chapter.

Recent work on the temperature coefficient of the conductivity of ammonia has brought out an interesting fact. Goodwin and Thompson found the coefficient to be about 0.011, while Frenzel, with a much purer sample, found it to be considerably higher than this (see Table 9). Consequently, the temperature coefficient of pure ammonia like that of pure water is greater than the coefficient of the slightly impure liquid.

The influence of small quantities of water on the conductivity of liquid ammonia has been investigated by Cady and by Frenzel.

[1] *Ztschr. phys. Chem.*, 28, 22-23 and 26-27 (1898).
[2] *Ibid.* 28, 619 (1899).
[3] *Ibid.*, 46, 131 (1903).

Cady found this influence to be slight, but the ammonia which he employed, as shown by its conductivity, was undoubtedly not pure. Frenzel's results, with a very pure sample, are given below. They show the effect on the conductivity of 4 cc. ammonia of adding the quantities of water given in the first column. The effect is

| Water added. Mg. | Conductivity at $-60°$. $K \times 10^6$. |
|---|---|
| 0.0 | 0.3549 |
| 1.4 | 0.6051 |
| 1.4 | 0.9966 |
| 2.8 | 1.996 |

seen to be quite marked and contradicts entirely Cady's conclusions. When this is, however, compared with the effect of small quantities of $CO_2$ and $NH_3$ on the conductivity of water it cannot be considered to be exceptional.

**CONDUCTING AND NON-CONDUCTING LIQUIDS.**—There seem to be no constitutional characteristics which distinguish inorganic liquids that conduct electricity from those that are non-conductors. A list of most of those that conduct has already been given in the table. According to Walden the following are non-conductors:[1] Antimony pentachloride, boron trichloride, bromine, phosphorus tribromide and trichloride, disulphur dichloride, sulphur trioxide and tin tetrachloride. Frankland and Farmer[2] have found nitrogen peroxide to be a non-conductor, and liquid hydrogen sulphide does not conduct according to Skilling.[3] Whether a substance is saturated or unsaturated appears to make no difference in its conducting power. It may be said that all those compounds which conduct contain as their principal element a member of the fifth or sixth groups of the periodic system. But, on the other hand, a number of substances are non-conductors which contain such an element.

Of the organic liquids the following may be said, speaking generally, to be non-conductors: Hydrocarbons, their halogen substitution products and the ethers. Those that conduct are alcohols, aldehydes, acids, esters, nitriles, nitro-compounds and ammonia substitution products. General constitutional differences

[1] Most of these have been investigated qualitatively much earlier. See Ostwald *Lehrbuch. d. Allg. Chemie*, 2, 1, 776.

[2] *J. Chem. Soc.*, 79, 1356 (1901).

[3] *Am. Chem. J.*, 26, 383 (1901).

distinguishing conductors from non-conductors are, therefore, found among organic compounds, which are lacking in the case of inorganic. But even here the line of demarcation is not hard and fast. Furthermore, any class of compounds which may be designated as conductors, gradually loses this property as the number of carbon atoms increases, so that the higher members of the series are non-conductors.

**CONDUCTIVITY OF FUSED ELECTROLYTES.**—Fused electrolytes conduct electricity well. Bouty and Poincaré[1] have devised an excellent method for determining the conductivity of fused salts. As used by Poincaré,[2] to determine the conductivity of a number of such salts under different conditions, it consisted essentially in using silver electrodes and to prevent polarization adding to the fused electrolyte a small quantity of that silver salt having the same anion. Only an extremely small quantity of the silver salt is required, not enough to affect appreciably the value of the conductivity of the electrolyte.

Some of the regularities observed by Poincaré are the following: (1) The conductivity increases with the temperature. (2) The conductivities of similar salts, as, for instance, the halogen salts of any one metal, have nearly equal values at equal distances from their fusing-points. For example, the molecular conductivity of NaCl, NaBr and NaI at 50° above the melting-point of each is 120.6, 124.0 and 123.6, respectively. However, this apparent regularity is not to be unduly emphasized without additional evidence. (3) The conductivity of mixtures of fused salts is practically additive, that is, is approximately the sum of the conductivities of the components.

**CONDUCTIVITY OF SOLID ELECTROLYTES.**—Many salts possess a considerable conductivity below their points of fusion, as has been observed by W. Kohlrausch[3] and also by Graetz.[4] Fritsch[5] has shown that this conductivity is greatly increased by the presence of small quantities of other solid substances as impurities, such mixtures acting apparently as solutions of the im-

[1] *Ann. chim. phys.*, (6) 17, 52 (1889).
[2] *Ibid.*, (6) 21, 289 (1890).
[3] *Wied. Ann.*, 17, 642 (1882).
[4] *Ibid.*, 40, 18 (1890).
[5] *Ibid.*, 60, 300 (1897).

purity in the solid salt. The following figures show the effect of the addition of from 1 to 2 per cent. of KBr to solid AgBr. The conductivity is expressed in arbitrary units.

| Experiment number | Conductivity AgBr | Conductivity after addition of KBr |
|---|---|---|
| 1 | 40 | 50 |
| 2 | 32 | 190 |
| 3 | 52 | 108 |
| | After standing 1 day | 211 |
| | 1½ days | 270 |
| | 2 days | 550 |

The increase of the conductivity on standing was probably due to more thorough diffusion of the impurity. The conductivity of both pure substances and of mixtures was also found to increase rapidly with the temperature. The conductivity of $SiO_2$, in distinction from that of salts, increased very little on the addition of such impurities as metallic oxides and KF. No effect could be observed on the conductivity of metallic oxides by the addition to them of other metallic oxides.

**WHY DO PURE LIQUIDS CONDUCT ELECTRICITY?**—In accordance with the dissociation theory it is assumed that the conductivity of pure liquids and also of fused salts is due to self-ionization, that is, that a small portion of the substance is dissociated into ions in a manner similar to the dissociation of substances in solution. Many liquids that conduct electricity are associated, however, that is, in the liquid state their molecular weight is greater than the simple formula which expresses the molecular weight in the gaseous condition. This is true of water. Nevertheless there are good grounds for assuming that some few of these associated molecules are broken down into the simple ones, and that an exceedingly small number of these dissociate into the ions H and OH. The reason for this assumption, beyond the fact that water is a conductor, are based mostly on results obtained from the investigation of electromotive forces, especially of gas cells and of neutralization cells. From the latter it is estimated that the number of gram-ions of hydrogen in a liter of water is $0.8 \times 10^{-7}$, a value which agrees well with that calculated by Kohlrausch from the conductivity.

Other liquids are supposed to dissociate in a somewhat similar

manner. Frenzel,[1] in measuring the electromotive force of polarization in liquid ammonia, found at the anode three decomposition points, hence he believes that pure $NH_3$ dissociates in three stages: Some molecules are dissociated into H and $NH_2$, then some few of the latter undergo further dissociation into H and NH, and an exceedingly small number of NH ions into H and N.

Walden[2] assumes dissociation of the organic liquids investigated by him into definite ions without, however, anything to guide him except analogy and conjecture.

Quite recently Bottomley[3] has shown that the molecular constitution of fused salts does not differ greatly from that of ordinary liquids. He finds, by the Ramsay and Shields' method, that fused sodium nitrate and fused potassium nitrate are associated substances, the molecular weights being about ten times that of the simple formulas. The conductivity of such salts is, therefore, probably due to the partial dissociation of these complex molecules into simpler ones, and possibly some of these are dissociated into the ions Na and $NO_3$, or into K and $NO_3$, or possibly the ions are much more complex, as seems to be the case in concentrated solutions of strong electrolytes.

[1] *Ztschr. Elektrochem.*, 6, 493 (1900).
[2] *Ztschr. phys. Chem.*, 46, 103 (1903).
[3] *J. Chem. Soc.*, 83, 1421 (1903).

## CHAPTER XIII.

### Non-aqueous Solutions.

**INTRODUCTION.**—Our theories of solution, which have been founded for the most part on the conduct of aqueous solutions, have lately been subjected to close scrutiny in attempts to apply them to non-aqueous solutions. It has, at least, been shown that these theories cannot be extended without modification into this field, opinions differing, however, as to the degree of modification which they must undergo. Some are already reading the obituary of the present theories, while others, less radical, believe they will be found adequate after certain important, but by no means fatal, modifications.

All this has served to stimulate investigation into the properties of non-aqueous solutions and especially into the electrical conductivity, so that data on this subject have increased more than fourfold within the last five years. Much must, however, still be done before it will be possible to reach a satisfactory explanation of the phenomenon of solution in general.

**CONDUCTIVITY OF NON-AQUEOUS SOLUTIONS.**—The methods employed in measuring the conductivity of non-aqueous solutions are entirely similar to those described in the case of non-aqueous liquids (page 128) with such modifications as are required by solutions. Special attention must be given to the dilution of such solutions[1] for the reason that the volume undergoes greater changes, both with the temperature and with the concentration, than is the case with aqueous solutions.

In general, those liquids which yield solutions that conduct are themselves conductors, and the conductivity of by far the greater number of such solutions is very much less than that of the corresponding aqueous solutions. When the solvent is an organic substance the conductivity is almost invariably less than that of aqueous solutions, but when the solvent is inorganic—including here HCN—the conductivity is, in many instances, greater. A few examples will illustrate the great variety of cases met with. In the tables the equivalent conductivity is given in reciprocal

[1] See Cohen, *Ztschr. phys. Chem.*, **25**, 1 (1898).

ohms. In most cases a recalculation was necessary, as the conductivity had been expressed in reciprocal mercury units. Where it has materially aided comparison, the conductivity has been interpolated from the values given by the individual investigators to values at dilutions which are powers of 2. The authorities are given in parenthesis.

CONDUCTIVITY OF ELECTROLYTES IN INORGANIC SOLVENTS (INCLUDING HCN AND $(CH_3)_2SO_4$)

Ammonia.

| (F. & K.) −38°. | | | | | | (G. & T.) −15°. | |
|---|---|---|---|---|---|---|---|
| v. | Λ. KBr. | v. | Λ. AgI. | v. | Λ. $Hg(CN)_2$. | v. | Λ. $AgNO_3$. |
| 301.9 | 210.6 | 212.1 | 71.1 | 6.92 | 1.44 | 30 | 143 |
| 625.9 | 242.3 | 439.8 | 96.3 | 14.35 | 1.30 | 54 | 163 |
| 1354 | 272.9 | 951.3 | 122.7 | 29.17 | 1.23 | 64 | 174 |
| 2824 | 299.8 | 1985 | 155.5 | 39.28 | 1.22 | 79 | 182 |
| 5740 | 317.6 | 4034 | 188.2 | 120.5 | 1.20 | 94 | 188 |
| 12410 | 329.7 | 8724 | 221.1 | 244.9 | 1.19 | 110 | 192 |

Hydrocyanic Acid.

| (Cent.) 0°. | | | (K. & S.) 0°. | | | Sulphur Dioxide. (W. & C.) 0°. | | | |
|---|---|---|---|---|---|---|---|---|---|
| v. | Λ. KI. | Λ. $S(CH_3)_2I$. | Λ. KI. | v. | Λ. $AgNO_3$. | v. | Λ. KI. | Λ. $N(CH_3)_4I$. | Λ. $NH_4CH_3Cl$. |
| 16 | 264 | 276 | 263 | 31.1 | 16.0 | 8 | 37.9 | 88.6 | 7.9 |
| 32 | 272 | 292 | 282 | 104.8 | 17.5 | 16 | 39.4 | 91.4 | 8.6 |
| 64 | 279 | 304 | 298 | 392.0 | 24.7 | 32 | 44.0 | 96.6 | 10.1 |
| 128 | 286 | 313 | 308 | | | 64 | 51.5 | 104.4 | 12.9 |
| 256 | 294 | 320 | 316 | | | 128 | 61.5 | 118.9 | 16.9 |
| 512 | 301 | 327 | 323 | | | 256 | 75.1 | 133.8 | 22.6 |
| 1024 | 308 | 332 | | | | 512 | 92.4 | 157.1 | 30.4 |
| | | | | | | 1024 | 112.5 | 167.7 | 40.6 |
| | | | | | | 2048 | 134.5 | | 55.5 |

$N(C_2H_5)_4I$ in Different Inorganic Solvents

(Walden.)

| v. | $SO_2$. | $AsCl_3$. | Λ. 25°. $(CH_3)_2SO_4$. | $POCl_3$. | $SOCl_2$. | $SO_2Cl_2$. | Λ. 33°. $AsBr_3$. |
|---|---|---|---|---|---|---|---|
| 200 | 132.2 | | 33.6 | | | | 15.0 |
| 250 | 135.9 | 55.1 | 33.8 | 30.8 | 20.7 | 17.1 | |
| 500 | 150.4 | 57.9 | 35.4 | 37.5 | 27.1 | 20.9 | 19.4 |
| 750 | 158.6 | 59.7 | 37.4 | 38.5 | 30.9 | 23.6 | |
| 1500 | 172.1 | 63.2 | | 44.3 | | | |

(Walden.) 25°.

| $BaSO_4$ in $H_2SO_4$. | | KBr in $HClSO_3$ | |
|---|---|---|---|
| v. | Λ. | | |
| 8 | 55.7 | | |
| 16 | 47.2 | | |
| 32 | 35.2 | | |
| | | 146 | 23.5 |
| | | 490 | 20.6 |

CONDUCTIVITY OF ELECTROLYTES IN ORGANIC SOLVENTS.

Methyl alcohol

| | (Carrara) 25°. | | (J. & L.) 25°. |
|---|---|---|---|
| v. | KI. | LiCl. | ½SrI₂. |
| 16 | 72.6 | 51.2 | 54.0 |
| 32 | 79.3 | 57.9 | 61.5 |
| 64 | 85.0 | 63.5 | 68.5 |
| 128 | 90.3 | 68.1 | 75.4 |
| 256 | 94.0 | 71.4 | 82.0 |
| 512 | 96.8 | 74.3 | 88.6 |
| 1024 | 99.1 | 77.8 | |
| 2048 | | 79.8 | |

Ethyl alcohol

| | (Völlmer) 18°. | | (Cohen) 18°. | (J. & L.) 25°. |
|---|---|---|---|---|
| v. | LiCl. | AgNO₃. | KI. | ½SrI₂. |
| 16 | 15.6 | ... | ... | 12.8 |
| 32 | 18.3 | 13.1 | ... | 15.4 |
| 64 | 20.7 | 17.5 | 27.8 | 17.9 |
| 128 | 23.3 | 21.0 | 31.1 | 20.7 |
| 256 | 25.9 | 24.2 | 33.9 | 24.5 |
| 512 | 27.9 | 27.5 | 36.7 | 27.3 |
| 1024 | 29.7 | 30.4 | 38.4 | |
| 2048 | 31.2 | 33.0 | 38.7 | |

Propyl alcohol.

| | (Schlamp) 15.2°. | | (J. & L.) 25°. |
|---|---|---|---|
| v. | NaI. | LiCl. | ½SrI₂. |
| 8 | 7.1 | 4.1 | .. |
| 16 | 8.1 | 5.1 | 4.0 |
| 32 | 9.2 | 6.1 | 4.7 |
| 64 | 10.6 | 7.3 | 5.4 |
| 128 | 12.0 | 8.8 | 6.0 |
| 256 | 13.4 | 10.2 | |
| 512 | 14.7 | 11.5 | |
| 1024 | 15.9 | 12.7 | |
| 2048 | 17.0 | 13.5 | |

Amyl alcohol.

| (A. & H.) 25°. |
|---|
| LiCl. |
| 0.65 |
| 0.74 |
| 0.86 |
| 1.10 |
| 1.43 |
| 1.84 |
| 2.37 |
| 3.06 |
| 3.73 |

Isoamyl alcohol.

| (Kablukoff) 25°. | |
|---|---|
| v. | HCl. |
| 3.42 | 1.91 |
| 5.44 | 1.77 |
| 8.93 | 1.57 |
| 14.29 | 1.51 |
| 25.42 | 1.33 |

Formic acid.

| | (Z.-T.) 25°. | | |
|---|---|---|---|
| v. | KCl. | v. | HCl. |
| 32 | 43.4 | 2.93 | 31.6 |
| 64 | 46.4 | 5.86 | 32.8 |
| 128 | 51.9 | 11.72 | 32.7 |
| 256 | 58.0 | 23.45 | 32.6 |
| 512 | 61.1 | 46.90 | 33.2 |

Acetone

| | (Lasczynski) 18°. | | | | |
|---|---|---|---|---|---|
| v. | KI. | v. | LiCl. | v. | AgNO₃. |
| 144.7 | 116.6 | 12.44 | 4.88 | 143.9 | 14.2 |
| 289.4 | 128.3 | 24.88 | 7.05 | 287.8 | 15.7 |
| 578.8 | 145.2 | 49.76 | 10.02 | 575.6 | 17.6 |
| 1157.6 | 155.4 | 99.52 | 13.8 | | |
| 2315.2 | 163.3 | | | | |

**Acetonitrile.**

(D. & F.) 25°.

| v. | Λ LiCl. | Λ $AgNO_3$. |
|---|---|---|
| 8 | ... | 58.1 |
| 16 | ... | 76.0 |
| 32 | 18.7 | 93.7 |
| 64 | 23.8 | 110.5 |
| 128 | 30.0 | 126.1 |
| 256 | 37.0 | 140.2 |
| 512 | | 154 |
| 1024 | | 167 |

**Propionitrile.**

(D. & F.) 25°.

| v. | Λ $AgNO_3$. |
|---|---|
| 32 | 37.2 |
| 64 | 49.0 |

**Butyronitrile.**

(D. & F.) 25°.

| v. | Λ $AgNO_3$. |
|---|---|
| 64 | 25.5 |
| 128 | 32.4 |

**Benzonitrile.**

(Lincoln) 25°.

| v. | Λ $AgNO_3$. |
|---|---|
| 8 | 5.1 |
| 16 | 6.8 |
| 32 | 9.3 |
| 64 | 12.7 |
| 128 | 16.3 |
| 256 | 18.9 |
| 512 | 21.6 |
| 1024 | 24.3 |

**Pyridine.**

(L. & G.) 25°.

| v. | Λ KI. | Λ LiCl. |
|---|---|---|
| 32 | ... | 1.49 |
| 64 | ... | 1.96 |
| 128 | 21.5 | 2.73 |
| 256 | 25.8 | 4.05 |
| 512 | 30.2 | |
| 1024 | 34.6 | |
| 2048 | 38.7 | |

(Lincoln) 25°.

| v. | Λ $AgNO_3$. |
|---|---|
| 10.71 | 24.4 |
| 25.52 | 28.7 |
| 37.32 | 29.8 |
| 60.90 | 32.2 |
| 140.57 | 38.6 |
| 392.28 | 42.8 |
| 784.56 | 48.2 |

**Quinoline.**

(Lincoln) 25°.

| v. | Λ $AgNO_3$. |
|---|---|
| 4.80 | 2.61 |
| 9.60 | 2.97 |
| 34.92 | 2.99 |
| 129.83 | 3.86 |

**Piperidine.**

(Lincoln) 25°.

| v. | Λ $AgNO_3$. |
|---|---|
| 4.24 | 0.39 |
| 5.25 | 0.30 |
| 7.88 | 0.16 |
| 10.50 | 0.10 |
| 15 62 | 0.05 |


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Z-T., Zanninovich-Tessarin, *Ibid.*, 19, 251 (1896).


**DISCUSSION OF RESULTS.**—In general, solutions in ammoni sulphur dioxide and hydrocyanic acid conduct electricity we The values of the equivalent conductivity are, in many cases, eve

greater than those of the same electrolytes in aqueous solutions at ordinary temperature. It must, however, be borne in mind that at the temperatures, at which these measurments were made, the above solvents are either at their boiling-points or very close to them. In order, therefore, that the physical conditions of the solvents may be more nearly uniform, these conductivities should be compared with those of the corresponding aqueous solutions measured near the temperature of boiling water. Kahlenberg has determined the conductivity at 95° of a number of substances dissolved in water. From an examination of his results (see appendix) it is seen that the equivalent conductivity of a substance at 95° is more than three times as great as at 18°. It is also considerably greater at the same concentration than that of the same electrolyte dissolved in the non-aqueous solvents in question. The reason of this increase in the conductivity of a solution at temperatures near the boiling-point of the solvent has been discussed elsewhere, and is undoubtedly due principally to increased speed of the ions on account of the diminished viscosity of the solvent rather than to increased dissociation of the electrolyte.

Solutions of tetraethylammonium iodide in $SO_2$, $AsCl_3$, $(CH_3)_2SO_4$, $POCl_3$, $SOCl_2$, $SO_2Cl_2$ and $AsBr_3$ conduct fairly well. Solutions in $SbCl_3$ conduct about as well as those in $AsCl_3$. Walden[1] points out in his first paper that solutions in these liquids—with the exception of those in $SO_2$ and those in $AsBr_3$, which had not been investigated at that time—conduct electricity, roughly speaking, in the same order in which the pure solvents conduct. He also calls attention to the fact that those inorganic solvents which yield conducting solutions are compounds of elements of the fifth and sixth groups of the periodic system. These elements are:

| Group V. | Group VI. |
|---|---|
| N | O |
| P | S |
| As | |
| Sb | |

But, as has already been said, the converse is not true, for substances very similar in nature to those which yield conducting

[1] *Zeitschr. anorg. Chem.*, 25, 225 (1900).

solutions neither conduct themselves nor do their solutions conduct. It may be said, however. that, in general, those liquids, which are themselves conductors, yield solutions that conduct.

The conductivity of alcoholic solutions steadily diminishes with increase in the atomic weight of the alcohol, so that, although solutions in methyl alcohol conduct well, those in amyl alcohol conduct but feebly. The same is true of the members of any homologous series whose solutions conduct, that is, that increase in the number of carbon atoms in the molecules of the solvent is always attended by a decrease of the conductivity of solutions in that solvent. The nitrites serve as a further illustration of this. Furthermore, solutions in pyridine are seen to conduct quite well, while those in piperidine and in quinoline are rather poor conductors. Solutions in acetone seem to be, in general, good conductors, as is seen in the case of KI, which conducts better than when dissolved in the alcohols. The conductivity of LiCl and of $AgNO_3$, however, is much less in acetone than when dissolved in either methyl or ethyl alcohol. Similar irregularities in the conductivity of the same electrolyte in different solvents are frequently met with. It cannot, therefore, be inferred that the conductivity of a certain electrolyte in one solvent will be greater than in another, simply because the conductivity of some other electrolyte is greater when dissolved in the first solvent than when dissolved in the second.

In nearly every instance the equivalent conductivity increases with the dilution as it does in the case of aqueous solutions. There are, however, some exceptions to this, as can be observed above in the cases of mercuric cyanide in ammonia, hydrochloric acid in isoamyl alcohol and silver nitrate in piperidine. A few other examples of the same kind can be found scattered through the literature of this subject. The significance of such conduct is not yet clearly understood.

It has been found that the alkali metals dissolve in liquid ammonia and that the solutions so formed conduct electricity well, and, what is more remarkable, without polarization. For a discussion of this interesting subject reference is made to the work

of Franklin and Kraus.[1] The same investigators[2] have also found that sulphur dissolves in ammonia, and that the resulting solution conducts fairly well. Walden[3] has recently shown that solutions of bromine in sulphur dioxide and iodine in sulphuryl chloride are conductors.

**INFLUENCE OF TEMPERATURE ON THE CONDUCTIVITY OF NON-AQUEOUS SOLUTIONS.**—We have already seen (Chapter IX) that, theoretically, the conductivity of aqueous solutions increases with rise of temperature, reaches a maximum, and then decreases. The effect of change of temperature on the conductivity of non-aqueous solutions appears to be similar. Whether the temperature coefficient of the conductivity of a solution is positive or negative, therefore, depends on the nature of that portion of the temperature curve at which the conductivity is being investigated. The negative temperature coefficients, found by Cattaneo[4] for ethereal solutions, are to be thus explained. In fact, Eversheim[5] has recently shown that the conductivity of HCl in ether is a maximum at —20°.

The conductivity of solutions in the following solvents has been investigated at the critical temperature: In ammonia by Franklin and Kraus;[6] in sulphur dioxide by Hagenbach;[7] and by Walden and Centnerszwer;[8] in sulphur dioxide, in ether and in chlorethane by Eversheim;[5] in methyl and in ethyl alcohol by Kraus.[9] In all these cases it was found that the conductivity passes through a maximum and then decreases towards the critical temperature, at which point it becomes very small. Walden and Centnerszwer infer that conductivity ceases altogether at the critical temperature, but this view is not shared by the other investigators. In fact, the recent work of Kraus appears to afford conclusive evidence that it is not so, for solutions in methyl alcohol possess a considerable conductivity above this temperature,—

[1] *Am. Chem. J.*, 23, 306 (1900).
[2] *Ibid.*, 24, 89 (1900).
[3] *Ztschr. phys. Chem.*, 43, 385 (1903).
[4] *Wied. Beibl.*, 17, 1085 (1893).
[5] *Drud. Ann.*, 8, 539 (1902).
[6] *Am. Chem. J.*, 24, 83 (1900).
[7] *Drud. Ann.*, 8, 276 (1901).
[8] *Ztschr. phys. Chem.*, 39, 538 (1902).
[9] *Phys. Rev.*, 18, 40 and 89 (1904).

more than can possibly be accounted for by any experimental errors. Kraus, however, finds that the temperature coefficient undergoes a sudden change at the critical temperature, which can be readily recognized by plotting the conductivities in a curve.

Although the changes which the conductivity of non-aqueous solutions undergoes with the temperature follow, in a general way, Arrhenius' theory (see page 100), his formula, as Eversheim points out, by no means applies to the particular cases which have been investigated.

**DISSOCIATION OF ELECTROLYTES IN NON-AQUEOUS SOLUTIONS.**—It has already been stated that the theory most generally adopted to account for the conductivity of aqueous solutions is that some of the molecules of the electrolyte, the so-called active portion, are dissociated into particles called ions. The question therefore arises whether the same hypothesis will afford an equally adequate explanation of the conductivity of non-aqueous solutions.

From the investigations of this subject, reported for the most part in the articles cited in the course of the presentation of the foregoing results, the following facts may be gathered.

(1) In the majority of instances the equivalent conductivity increases with the dilution, but a maximum value can be even approximately estimated in but few instances, which are chiefly found in alcoholic solutions.[1]

(2) The molecular weight of the solute in dilute aqueous solutions which conduct well, when determined by the freezing point or boiling point method, is in nearly every case considerably less than the true molecular weight. In non-aqueous solutions this is not so frequently the case. It is true in general of most alcoholic solutions, but more usually not true of non-alcoholic solutions. In fact, in many such solutions which conduct well, the molecular weight of the solute is found to be greater than normal, showing that the electrolyte is polymerized rather than dissociated. As examples of this behavior may be cited potassium iodide in sulphur dioxide and hydrochloride acid in formic acid, which are seen according to the above table to be good conducting solutions.

[1] Values have been given to $\Lambda_\infty$ of many electrolytes in other non-aqueous solvents without the data, however, warranting it.

The molecular weights of the electrolytes in both these instances have been found by the freezing point method to be just about twice the normal values.

(3) Since it is impossible to estimate the value of $\Lambda_\infty$ with any degree of accuracy for most non-aqueous solutions, it is of course impossible to calculate the ratio, $\frac{\Lambda_v}{\Lambda_\infty}$, or the degree of dissociation. In the cases where it is possible to estimate $\Lambda_\infty$, the degree of dissociation thus calculated has seldom been found to agree with that calculated from determination of the freezing point or boiling point of the solution. However, with electrolytes in methyl alcohol or in ethyl alcohol the agreement can in many instances be considered to be good.

(4) Ostwald's dilution law (Chapter 6), which we have seen holds for aqueous solutions of weak electrolytes, does not hold in most cases where it is possible to apply it to non-aqueous solutions. In alcoholic solutions, where the degree of dissociation can quite generally be determined and consequently the applicability of the law tested, in the majority of cases it does not hold. Some instances where it has been found to hold are for trichloracetic acid in ethyl alcohol and for potassium chloride in formic acid[1].

(5) Kohrausch's law of the independent migration of the ions cannot of course be adequately tested where it is impossible to estimate accurately $\Lambda_\infty$. According to Carrara it holds roughly for most electrolytes dissolved in methyl or in ethyl alcohol, and he has prepared a table of migration numbers of the ions in these solvents.

From this brief summary of the facts at present known, it may be said that the conduct of electrolytes in alcoholic solutions bears the greatest resemblance to that in aqueous solutions, and in such solutions dissociation into ions very similar in kind to that in water probably takes place. This similarity in conduct to aqueous solutions decreases with increase in the molecular weight of the alcohol, so that amyl alcohol solutions have practically lost this resemblance. Electrolytes in most other solvents show but little evidence of dissociation of a kind similar to that which takes place in dilute aqueous solutions. It has been stated that electrolytes in non-aqueous solutions appear to be very generally

[1] Other instances have recently been found by Godlewski, Ref. Central-B., 1904, II, 1275.

polymerized. These polymerized molecules may be made up by the aggregation of two or more molecules of the solute, or may be formed by the union of one or more molecules of the solute with one or more molecules of the solvent. Evidence that a union of this last sort sometimes takes place lies in the fact that heat is evolved when some substances are dissolved in certain solvents, for example silver nitrate in pyridine. Doubtless the former, that is true polymerization of the solute, also actually takes place in some instances. Such behavior is not entirely foreign to aqueous solutions, as for instance solutions of cadmium salts. But in such cases the decomposition of the polymerized molecules takes place rapidly on diluting the solution, so that in solutions whose concentration is not greater than $^1/_{100}$ normal all evidence of polymerized molecules and even of complex ions has disappeared. (See discussion under transport numbers of bivalent ions, Chapter 7). This is, however, very different from the conduct of most non-aqueous solutions; for, although the polymerized molecules seem to be somewhat broken up on dilution, this procedure is very slow; and it is doubtful, if in many cases any evidence can be found for the existence of particles smaller than normal molecules, that is, particles of the same kind as the ions of dilute aqueous solutions.

Walden[1], however, in a recent article is strongly of the belief that all electrolytes undergo dissociation no matter what the solvent may be, though the ions may differ in different solvents. The next question then is to determine what ions are present in a given case. Without any direct evidence he assumes in each case dissociation of a kind which appears to him to be most probable under the given conditions. For example, he ascribes the conductivity of bases like pyridine when dissolved in sulphur dioxide to the formation of complex molecules $R \equiv N = S\begin{matrix}O\\O\end{matrix}$, in the case of pyridine, $C_5H_5N = S\begin{matrix}O\\O\end{matrix}$, which dissociates into the cation $\overset{+}{R} \equiv \overset{+}{N}$ and into the anion, $\overset{- -}{SO_2}$.

[1] *Zischr. phys. Chem.*, 43, 385 (1903).

Before leaving this subject another striking difference between the behavior of aqueous and some non-aqueous solutions should be mentioned. This is the fact that the equivalent conductivity of some electrolytes in certain non-aqueous solvents decreases on dilution, while no example of this kind is known among aqueous solutions. The significance of such conduct is not clearly understood.

In conclusion it may be stated that electrolytic dissociation of the same kind as that which takes place in water, if it occurs at all in non-aqueous solvents, occurs probably in methyl and ethyl alcohols, and it is interesting to note that these liquids resemble water constitutionally in that each contains an hydroxyl group. Formic acid, whose solutions show some similarity to aqueous solutions, also contains an hydroxyl group. Our knowledge of dissociation in other solvents is so limited that we are scarcely warranted in drawing any general conclusions concerning its nature.[1]

**INFLUENCE OF THE SOLVENT ON THE CONDUCTIVITY OF SOLUTIONS.**—The condition of the electrolyte in non-aqueous solutions has just been discussed. Undoubtedly, however, the conductivity of a solution depends to a great extent also on the nature of the solvent; for HCl, which is a good conductor in many solvents, when dissolved in benzene does not conduct at all. The question then arises, what is there in the nature of a solvent which causes it to yield solutions that conduct electricity.

(1) The first explanation offered in answer to this question was stated independently by Thomson[2] and by Nernst[3]. They suggested that the power to yield conducting solutions depends on the specific inductive capacity of the solvent, and consequently the greater the dielectric constant of a solvent the greater the conductivity of substances dissolved in it. The idea which led up to this rule was, that solvents having high dielectric constants render it more difficult for the charges on oppositely charged ions to neutralize each other on account of the electrostatic attraction

[1] Besides Walden's paper just cited, the following paper by Whetham should be consulted in this connection: *Phil. Mag.*, (5) 8, 279 (1903).

[2] *Phil. Mag.*, (5) 36, 320 (1893).

[3] *Ztschr. phys. Chem.*, 13, 531 (1894).

existing between them. Nernst showed that there was a distinct parallelism between the electrolytic conductivity of a solution and the dielectric constant of the solvent, as far as the data on the conductivity of electrolytes in different solvents extended at that time. He furthermore pointed out that this parallelism is only relative, that is, that conducting power and dielectric constant are not in strict proportion. An absolute parallelism was hardly to be expected, because other factors undoubtedly also have some influence.

Recent experimental data have, however, brought to light numerous exceptions to this rule. Liquid ammonia has a much smaller dielectric constant (16) than hydrocyanic acid (95) or water (81), but its solutions conduct on an average as well as those in the latter liquids. Sulphur dioxide also yields solutions which are excellent conductors, but its dielectric constant is only 14. Solutions of KI in acetone (D. C., 21) are much better conductors than solutions of the same salt dissolved in methyl or in ethyl alcohol (D. C., 32.5 and 27, respectively). However, there are other electrolytes which conduct better when dissolved in either of the two alcohols mentioned than when dissolved in acetone. Attention has already been called to this fact,—that is, that certain electrolytes may be better conductors when dissolved in one solvent than when dissolved in another, while certain others conduct better when dissolved in the second solvent than when dissolved in the first,—which of course shows that the Nernst-Thomson rule is not paramount in determining the power of a solvent to yield conducting solutions. It does, however, appear to be one of the influences affecting the conductivity of solutions, for when applied to solvents of similar constitution it seems to hold. The accompanying table gives the dielectric constants of four primary hydroxyl compounds and of three compounds containing the CN radicle. Conductivity measurements show that the conductivity of electrolytes dissolved in the solvents of either one of these series decreases as the dielectric constant decreases.

| Substance. | Dielectric constant. | Substance. | Dielectric constant. |
|---|---|---|---|
| Water | 81 | Hydrocyanic acid | 95 |
| Methyl alcohol | 32.5 | Acetonitrile | 40 |
| Ethyl alcohol | 27 | Propionitrile | 30 |
| Propyl alcohol | 20 | | |

Other explanations which have been proposed to account for the part played by the solvent in the conductivity of solutions will now be rapidly reviewed.

(2) Ciamician[1] has ascribed dissociative power to the chemical nature of the solvent, that is, to substances of certain distinctive types. For instance, solvents of the water type containing an hydroxyl group yield solutions which conduct, as do also solvents of the nitrile type containing the CN group. Although this rule seems to hold within limits for many organic solvents, it is entirely inadequate when applied to inorganic solvents, as their power to yield conducting solutions seems to be entirely independent of type.

(3) Konovaloff[2] thinks that only those solvents which react chemically with the solute yield solutions which conduct. Although there may be considerable truth in this general statement, when the exact nature of the reaction is considered, very little evidence of any uniformity has as yet been brought to light.

(4) Brühl[3] makes dissociative power depend on unsaturated chemical elements in the compound, for example such elements as N, O and S. He ascribes to oxygen a valence of 4. He himself admits that the presence of such an element in a substance does not necessarily imply that it will yield conducting solutions, so that the rule is of little value as a generalization.

(5) That a certain relation exists between the latent heat of vaporization of liquids, their dielectric constants, and their dissociative power has been pointed out by Obach[4] and further developed by Brühl[5].

(6) That there is a certain parallelism between the coefficients of association of solvents and their dissociative power was first called attention to by Crompton.[6] Dutoit, Aston and Friderich[7] have investigated this relation more fully, and they have also

[1] *Ztschr. phys. Chem.*, 6, 403 (1890). See also Cattaneo, *Rend Accad. Lincei.*, (5) 4, II, 63 (1895).

[2] *Wied. Ann.*, 49, 733 (1893).

[3] *Berichte*, 28, 2847 and 2866 (1895); 30, 163 (1897); *Ztschr. phys. Chem.*, 18, 514 (1895); 27, 319 (1898); 30, 3 (1899).

[4] *Phil. Mag.*, (5) 32, 113 (1891).

[5] *Ztschr. phys. Chem.*, 27, 319 (1898); 30, 42 (1899).

[6] *J. Chem. Soc.*, 71, 925 (1897).

[7] Dutoit and Aston, *Compt. Rend.*, 128, 240; Dutoit and Friderich, *Bul. Soc. chim.*, (3) 19, 321 (1898).

taken into consideration the coefficients of viscosity of the solvents in this connection. Their conclusions are, first, that electrolytes dissolved in non-polymerized solvents do not conduct, and secondly, that the value of $A_\infty$ of the same electrolyte in different solvents is a direct function of the degree of polymerization and an inverse function of the coefficient of viscosity of the solvent. In opposition to this view it may be said that pyridine whose coefficient of association is 0.93 yields solutions which conduct well, while electrolytes dissolved in ethylene chloride whose coefficient of association is 1.46 do not conduct at all. If it is held that only those substances are polymerized which possess residual affinities, the relation is at once apparent between this theory and that of Brühl.[1]

**SUMMARY.**—None of the above explanations is in itself adequate to account for all the facts which have been brought out in connection with the conductivity of solutions. Each one of them appears in the case of certain groups of solvents to be more or less related to the power to yield conducting solutions. This relation might be of a more general nature if the conductivity of the different solutions and the various physical constants of the solvents were determined under more uniform temperature conditions. The influence of temperature on conductivity has been already briefly discussed in this chapter, and it has been shown that the conductivity of a solution becomes very small at the critical temperature of the solvent. All of the physical constants of the solvent, which have been mentioned, vary considerably with the temperature, some of them becoming zero at the critical temperature. Consequently, if all these factors, including the conductivity itself, were investigated at equal fractions of the absolute critical temperature, the parallelism between them would very likely be increased. It is, however, extremely doubtful, whether even then strict proportionality could be found to exist between them.

The conductivity of a solution is apparently not to be referred to the nature of the solvent alone nor to the nature of the solute alone, but rather to the effect of their mutual interaction. Just what the interaction is when a conducting solution results remains

[1] For rather complete discussions of this subject see besides the papers already mentioned, Kohlenberg, *J. Phys. Chem.*, 5, 384 (1901); and Walden and Centnerswer, *Ztschr. phys. Chem.*, 39, 558 (1902).

yet to be explained. After this interaction has taken place we think we know something of the state of dilute aqueous solutions. Of the inner nature of concentrated aqueous solutions and of the majority of non-aqueous solutions we know on the other hand almost nothing, so that the general problem of the nature of solution remains as yet unsolved.[1]

**TRANSPORT NUMBERS IN NON-AQUEOUS SOLUTIONS.**—But few determinations of the relative velocities of the ions in non-aqueous solutions have been made. Hittorf[2] determined the transport numbers of $CdI_2$, $ZnCl_2$ and $ZnI_2$ in ethyl alcohol, and of $CdI_2$ in amyl alcohol, while Lenz[3] investigated $CdI_2$ in ethyl alcohol and also in mixtures of ethyl alcohol and water, and Campetti[4] LiCl and $AgNO_3$ in methyl and ethyl alcohols. More recently Mather[5] has determined the transport numbers of $AgNO_3$ in ethyl alcohol, and Schlundt[6] that of $AgNO_3$ in pyridine and in acetonitrile. Schlundt gives a table containing a resume of the results obtained with $AgNO_3$ in different solvents, which is reproduced below. The transport number of the cation is given.

TRANSPORT NUMBER OF THE CATION OF $AgNO_3$ IN DIFFERENT SOLVENTS.

| Solvent. | v = 0.42. | 1 | 2 | 4 | 10 | 16 | 35 | 40 |
|---|---|---|---|---|---|---|---|---|
| Water..... | 0.532 | 0.500 | 0.483 | 0.473 | .... | .... | .... | 0.475 |
| Acetonitrile .... | .... | 0.383 | .... | 0.422 | 0.448 | .... | 0.473 | .... |
| Pyridine ..... | .... | 0.326 | 0.342 | .... | 0.390 | .... | .... | 0.440 |
| Methyl alcohol . | .... | .... | .... | .... | .... | 0.533 | .... | .... |
| Ethyle alcohol . | .... | .... | .... | .... | 0.405 | 0.490 | .... | .... |

In the non-aqueous solvents the transport number of the cation increases with increasing dilution, while in water it decreases. This decrease of the transport number of the cation in aqueous solution has been explained by Noyes[7] on the assumption that complex anions exist in the more concentrated solutions, which gradually decompose on dilution. Correspondingly Schlundt sug-

[1] In a series of recent papers (*Am. Chem. J.*,) 31, 303 and 32, 308 (1904); *Ztschr. phys Chem.*, 49, 385 (1904)) Jones and Getman present evidence that the exceptional behavior of concentrated solutions is due to the presence of hydrates.

[2] *Pogg. Ann.*, 106, 551 (1859).

[3] See Ostwald's *Lehrbuch d. allg. Chemie*, II, 1, p. 618.

[4] *Nuovo Cimento*, 38, 226 (1894); Ref. *Ztschr. phys. Chem.*, 16, 165.

[5] *Am. Chem. J.*, 26, 473 (1901).

[6] *J. Phys. Chem.*, 6, 159 (1902).

[7] *J. Am. Chem. Soc.*, 23, 54 (1901).

gests that the change undergone on diluting solutions of $AgNO_3$ in pyridine and in acetonitrile is due to the existence of complex cations in the more concentrated solutions. The complex cation, he believes, however, is formed by some sort of combination between the $AgNO_3$ and the molecules of the solvent. This view is supported by the fact that heat is liberated when $AgNO_3$ is dissolved in these solvents. At any rate the nature of the solvent exercises considerable influence on the transport number of an electrolyte. This influence appears to be less, however, in very dilute solutions, since the values of the transport number found in the different solvents tend to approach one another as the dilution increases.

## CHAPTER XIV.

### Conductivity of Electrolytes in Mixed Solvents.

**RESEARCH OF ARRHENIUS.**—Investigations of the conductivity of electrolytes in mixed solvents have been almost entirely confined to ascertaining the effect on the conductivity of aqueous solutions produced by the addition of other solvents or *vice versa*. This is closely connected with the effect produced on the conductivity of aqueous solutions by adding solid non-electrolytes such as sugar and the like. When only small quantities of a non-aqueous solvent are added the effect produced is entirely similar in the two cases.

Arrhenius[1], who was the first to investigate this subject thoroughly, derived an empirical formula for calculating the change in conductivity of aqueous solutions due to additions of non-electrolytes. Starting from a general equation of the form,

$$l = l_0(1 - \alpha x + \beta x^2),$$

in which $l_0$ is the conductivity of the aqueous solution, $x$ the percentage concentration of the non-electrolyte and $\alpha$ and $\beta$ arbitrary constants, he finds the value of $\beta$ is given sufficiently accurately by making $\beta = \frac{x^2}{4}$. The equation then becomes

$$l = l_0(1 - \frac{\alpha}{2} x),^2$$

which contains only one arbitrary constant[2].

Arrhenius found that quantities of a non-conducting liquid not exceeding 10 per cent. of the total volume of the solution on being added to an aqueous solution of a good electrolyte decrease the conductivity nearly in proportion to the increase in the viscosity of the medium. $\alpha$ in the above equation represents the specific decrease for a 1 per cent. addition of the non-electrolyte. This quantity varies according to the nature of the electrolyte and of the non-electrolyte. It is, however, practically constant for certain types of electrolytes in the presence of the same non-electrolyte. For instance, for salts of the KCl type in the presence

[1] *Ztschr. phys. Chem.*, 9, 487 (1892).

[2] For further experimental work in connection with this formula, see Holland, *Wied. Ann.*, 50, 261 (1893), and Strindberg, *Ztschr. phys. Chem.*, 14, 161 (1894).

of ethyl alcohol the value of $\alpha$ varies but little from 0.0235. Since the conductivity decreases nearly in proportion to the increase in the viscosity of the solution, it indicates that the change in conductivity is largely due to the diminished speed of the ions rather than to change in the degree of dissociation of the electrolyte. In the case of strong electrolytes the latter is appreciably influenced only after the addition of the non-electrolyte considerably exceeds 10 per cent. With weak, electrolytes, however, it was found that the degree of dissociation is considerably affected from the start.

**EFFECT OF CHEMICAL UNION BETWEEN THE ELECTROLYTE AND THE NON-ELECTROLYTE.**—Hantzsch[1] has shown that when the non-electrolyte added has a tendency to form complex molecules with the electrolyte the equivalent conductivity is abnormally diminished, the effect being most marked when the non-electrolyte is present in exactly the right proportion to form the complex compound. The following results show the effect of adding different quantities of alcohol and of pyridine to $^1/_{20}$ normal solutions of potassium chloride and of silver nitrate. The coefficients before the formulas of alcohol and pyridine represent the number of molecules added to one molecule of the electrolyte. The conductivity has been recalculated to reciprocal ohms.

EFFECT ON THE CONDUCTIVITY OF KCl AND $AgNO_3$ SOLUTIONS OF ADDING ALCOHOL AND PYRIDINE.
Temperature 25°. $v = 20$ for all solutions.

| KCl | | $AgNO_3$ | |
|---|---|---|---|
| KCl | 131.8 | $AgNO_3$ | 116.5 |
| " + $4C_2H_6O$ | 129.0 | " + $2C_2H_6O$ | 103.8 |
| " + 6 " | 127.1 | " + 4 " | 102.9 |
| " + 8 " | 124.7 | | |
| " + 10 " | 122.2 | " + $2C_5H_5N$ | 81.1 |
| | | " + 4 " | 76.5 |
| " + $4C_5H_5N$ | 126.2 | " + 8 " | 71.0 |
| | | " + 20 " | 63.6 |

The effect on the conductivity is seen to be the greatest when pyridine is added to the solution of silver nitrate. This is in accord with the fact that heat is liberated when silver nitrate and pyridine are brought together, thereby showing that a chemical union takes place between them. The decrease is relatively the greatest when there are two molecules of pyridine to one mole-

[1] *Ztschr. anorg. Chem.*, 28, 332 (1900).

cule of silver nitrate, and this is the ratio in which these substances combine.

**CONDUCTIVITY OF ELECTROLYTES IN AQUEOUS ALCOHOLIC SOLUTIONS.**—The effect produced on the conductivity of aqueous solutions by adding ethyl alcohol has been frequently investigated. Wakeman[1] determined the conductivity of a number of substances when dissolved in mixtures of alcohol and water, especially with a view to finding whether the Ostwald dilution formula applied in such cases. He found that in general it did not hold. Roth[2] has since found that neither the formula of Ostwald, nor of van't Hoff, nor of Rudolphi, applied to the cases investigated by him, but that the following empirical formula of Kohlrausch could be used for interpolating with considerable success:

$$\frac{\Lambda_\infty - \Lambda}{\Lambda^p} = c\eta^{\frac{1}{2}}.$$

In this $p$ and $c$ are constants, which must be found experimentally from the data at hand.

Most of the investigators in this field have found that when the quantity of alcohol in the solution does not exceed 50 or 60 per cent.[3], the equivalent conductivity of dilute solutions of strong electrolytes as related to that of the corresponding aqueous solutions is dependent only on the amount of alcohol added and not on the concentration of the solution. This is illustrated by the following table taken from the paper of Cohen[4]. The conductivity has been recalculated to reciprocal ohms. In $A$ are given the equivalent conductivities at different dilutions of solutions of potassium iodide in water and in mixtures of alcohol and water, and in $B$ the conductivity of the aqueous solution at each dilution is made equal to 100 and the conductivities in the other solutions are given in relative terms.

[1] *Ztschr. phys. Chem.*, 11, 49 (1893).

[2] *Ibid.*, 42, 209 (1902).

[3] Throughout the consideration of aqueous alcohol solutions the concentration of the alcohol, unless otherwise indicated, is given in volume percentages.

[4] *Ztschr. phys. Chem.*, 28, 30 and 34 (1898).

EQUIVALENT CONDUCTIVITY. ELECTROLYTE, KCl. TEMPERATURE 18°.

| | Percentage alcohol. A. | | | | Percentage alcohol. B. | | | | |
|---|---|---|---|---|---|---|---|---|---|
| v. | 0. | 20. | 40. | 60. | v. | 0. | 20. | 40. | 60. |
| 64 | 121.4 | .. | 45.3 | 36.8 | 64 | 100 | .. | 37.3 | 30.3 |
| 128 | 124.0 | 70.6 | 46.4 | 37.8 | 128 | 100 | 56.9 | 37.4 | 30.5 |
| 256 | 125.7 | 71.1 | 46.6 | 38.4 | 256 | 100 | 56.6 | 37.0 | 30.5 |
| 512 | 127.5 | 72.0 | 47.2 | 39.1 | 512 | 100 | 56.5 | 37.0 | 30.7 |
| 1024 | 128.3 | 72.9 | 47.7 | 39.7 | 1024 | 100 | 56.8 | 37.1 | 30.9 |
| 2048 | 129.2 | 73.9 | 48.0 | 40.2 | 2048 | 100 | 57.1 | 37.1 | 31.1 |

The numbers in each column of table *B* are very nearly constant. They, however, show a slight tendency to increase at the higher dilutions, and in fact Roth from careful measurements with solutions of potassium chloride concludes that the relative conductivity is somewhat dependent on the percentage of alcohol as well as on the dilution[1]. His results follow:

EQUIVALENT CONDUCTIVITY. ELECTROLYTE, KCl. TEMPERATURE 18°

| | Solvent. | | | Conductivity in water = 100. | |
|---|---|---|---|---|---|
| v. | Water. | 10% alcohol. | 25% alcohol. | in 10% alchol. | in 25% alcohol. |
| 30 | 117.78 | 88.93 | 59.68 | 75.53 | 50.66 |
| 60 | 120.66 | 91.09 | 61.04 | 75.47 | 50.58 |
| 90 | 122.10 | 92.22 | 61.78 | 75.53 | 50.61 |
| 120 | 123.00 | 92.97 | 62.28 | 75.59 | 50.63 |
| 150 | 123.64 | 93.51 | 62.65 | 75.64 | 50.68 |
| 180 | 124.13 | 93.92 | 62.94 | 75.64 | 50.71 |
| 300 | 125.32 | 94.98 | 63.71 | 75.82 | 50.84 |
| 600 | 126.61 | 96.18 | 64.62 | 75.99 | 51.05 |

Here the numbers in the last two columns are nearly constant, a tendency to increase is however distinctly observed at the last two dilutions.

In solutions not so dilute but that the ratio of the conductivity in water to that in a mixture of alcohol and water is constant, the conductivity in a mixture of alcohol and water can be calculated from that in water alone by means of a factor depending only on the percentage of alcohol.

This factor seems to be influenced but little by the temperature or by the nature of the electrolyte—provided it belongs to the class of so-called strong electrolytes—as the following table shows. $F_{10}$, $F_{20}$, etc., indicate the factors by which the conductivity of the aqueous solutions are to be multiplied to give the conductivity of a solution containing a percentage of alcohol equal to 10, 20, etc., respectively.

[1] See in addition a more recent article by Shapire, supporting Roth; *Zischr. phys. Chem.*, 49, 513 (1904).

| Electrolyte. | Temperature. | $F_{10}$. | $F_{20}$. | $F_{30}$. | $F_{40}$. | $F_{50}$. |
|---|---|---|---|---|---|---|
| KI | 18° | .. | 0.57 | .. | 0.37 | .. |
| KI | 25 | 0.73 | 0.57 | 0.47 | 0.40 | 0.35 |
| KCl | 25 | 0.73 | 0.57 | 0.47 | 0.40 | 0.35 |
| NaCl | 25 | 0.75 | 0.59 | 0.49 | 0.41 | 0.37 |
| HCl | 25 | 0.75 | 0.60 | 0.48 | 0.40 | 0.32 |
| $NaC_2H_3O_2$ | 18 | .. | .. | .. | .. | 0.36 |

Walker and Hambly[1] have found practically the same to be true for the conductivity of diethylammonium chloride in aqueous alcohol up to 60 per cent. alcohol. In solutions containing more than 60 per cent. alcohol the factor was found to vary with the concentration, which they ascribed to a change in the degree of dissociation of the electrolyte.

Since, however, the factor is not constant at high dilutions, Roth infers that the speed of the ions is also affected by the addition of alcohol. Moreover, he finds that the temperature coefficients increase rapidly with increasing proportion of alcohol and increase slowly with the dilution. For considerable differences of temperature therefore, the factors would not be constant as the above table seems to indicate.

The transport numbers of some electrolytes in mixture of alcohol and water have been investigated by Lenz[2] and by some of Jahn's students.[3] The addition of alcohol to an aqueous solution of an electrolyte like KCl seems to decrease the transport number of the anion.

**AQUEOUS ALCOHOLIC SOLUTIONS OF MINIMUM CONDUCTIVITY.**—When small quantities of water are added to an alcoholic solution of KI, Cohen found the conductivity was affected in a rather remarkable manner. At dilutions of 64 liters the conductivity increased with the amount of water added, as was to be expected, but at dilutions greater than 512 liters the conductivity became less than that of the electrolyte in pure alcohol, as the following table shows. The measurements were made at 18°.

| | Percentage of Alcohol. | | |
|---|---|---|---|
| v. | 100. | 99. | 80. |
| 64 | 27.8 | 28.7 | 32.9 |
| 128 | 31.1 | 31.9 | 34.3 |
| 256 | 33.9 | 34.3 | 35.4 |
| 512 | 36.7 | 36.5 | 36.4 |
| 1024 | 38.4 | 37.7 | 36.8 |
| 2048 | 38.7 | 38.5 | 37.3 |

[1] *J. Chem. Soc.*, 71, 61 (1897).
[2] *Wied. Beibl.*, 7, 399 (1883).
[3] *Ztschr. phys. Chem.*, 37, 684 (1901). See also *Ibid.*, 42, 210 (1902).

More remarkable, however, is the behavior of aqueous methyl alcohol solutions in this respect as found by Zelinsky and Krapiwin[1]. The conductivity of the electrolytes, KBr, KI, $NH_4Br$, and $NH_4I$ in methyl alcohol is considerably less than in water. They found, however, that the addition of water, up to 50 per cent., to the solutions of these substances in methyl alcohol, instead of causing the equivalent conductivity to increase as might be expected, causes it to decrease for all concentrations investigated. The results obtained with solutions of KI and of $NH_4Br$ are given below by way of illustration. The figures have been recalculated to reciprocal ohms and represent equivalent conductivities at 25°.

CONDUCTIVITY OF KI AND $NH_4Br$ IN METHYL ALCOHOL, IN WATER, AND IN MIXTURES OF THE SAME.

| | Potassium Iodide. | | | | Ammonium Bromide. | | |
|---|---|---|---|---|---|---|---|
| | Percentage of Methyl Alcohol. | | | | | | |
| *v.* | 100 | 98 | 50 | 0 | 100 | 50 | 0 |
| 16 | 73.8 | 72.7 | 66.2 | 132.7 | 69.7 | 65.2 | 135.6 |
| 32 | 81.4 | 79.3 | 68.7 | 136.7 | 77.5 | 68.0 | 140.5 |
| 64 | 88.0 | 85.3 | 70.3 | 139.1 | 84.8 | 70.4 | 144.2 |
| 128 | 94.6 | 91.2 | 71.9 | 141.8 | 91.5 | 71.9 | 147.8 |
| 256 | 100.1 | 95.9 | 72.8 | 144.8 | 96.9 | 72.8 | 150.5 |
| 512 | 104.7 | 99.8 | 74.2 | 147 0 | 101.3 | 73.7 | 153.0 |
| 1024 | 108.9 | 102.6 | 75.2 | 150.2 | 104.7 | 74.7 | 155.2 |

Jones and Lindsay[2] have recently investigated the conductivity of a number of salts in water, in methyl alcohol, in ethyl alcohol, in propyl alcohol and in mixtures of some of these solvents. The measurements were made at both 0° and 25°. They have found a minimum conductivity for all salts investigated in aqueous methyl alcohol solution except for cadmium iodide, the conductivity of which was determined only at 25°. Mixtures of ethyl alcohol and water as solvent yield a minimum in the conductivity of all salts investigated at 0°. At 25° this minimum had disappeared, at least for 50 per cent. additions of water. The results obtained with lithium nitrate are given in the table below. These as well as all other of Jones and Lindsay's results reproduced in the following pages are expressed in equivalent conductivities and have been recalculated to reciprocal ohms.

[1] *Ztschr. phys. Chem.*, 21, 35 (1896).
[2] *Am. Chem. J.*, 28, 329 (1902).

CONDUCTIVITY OF $LiNO_3$ IN ETHYL ALCOHOL, WATER, AND A 50% MIXTURE OF THE SAME.

| | At 0°. | | | At 25°. | | |
|---|---|---|---|---|---|---|
| v. | Alcohol. | Mixture. | Water. | Alcohol. | Mixture. | Water. |
| 32 | 15.2 | 14.0 | 53.3 | 23.4 | 36.0 | 97.9 |
| 64 | 16.6 | 14.5 | 54.9 | 26.5 | 37.9 | 100.9 |
| 128 | 18.7 | 15.2 | 56.0 | 29.6 | 39.5 | 104.5 |
| 256 | 20.7 | 15.6 | 56.9 | 32.9 | 41.4 | 106.3 |
| 512 | 22.8 | 16.5 | 58.3 | 35.4 | 42.8 | 108.0 |
| 1024 | 24.8 | 17.3 | 59.0 | 37.9 | 44.1 | 109.0 |

The conductivity of the salts investigated in mixtures of propyl alcohol and water exhibit no minimum either at 0° or at 25°, as the following table shows.

CONDUCTIVITY OF $\frac{1}{2}SrI_2$ IN PROPYL ALCOHOL, WATER, AND A 50% MIXTURE OF THE SAME.

| | At 0°. | | | At 25°. | | |
|---|---|---|---|---|---|---|
| v. | Alcohol. | Mixture. | Water. | Alcohol. | Mixture. | Water. |
| 16 | 2.56 | 14.6 | 60.3 | 4.04 | 36.1 | 109.4 |
| 32 | 3.00 | 15.3 | 62.7 | 4.71 | 38.2 | 114.3 |
| 64 | 3.48 | 15.9 | 65.1 | 5.44 | 40.2 | 118.9 |
| 128 | 3.96 | 16.5 | 67.2 | 6.03 | 42.3 | 123.5 |

No point of minimum conductivity was found for salts dissolved in mixtures of methyl and ethyl alcohols, but the conductivity of a salt dissolved in a 50 per cent. mixture of these alcohols was found to be less than the mean of the conductivities of the salt dissolved in the two solvents separately. Jones and Lindsay's results with potassium iodide in methyl and ethyl alcohols are given in the accompanying table.

CONDUCTIVITY OF KI IN METHYL ALCOHOL, ETHYL ALCOHOL, AND A 50% MIXTURE OF THE SAME.

| | At 0°. | | | At 25°. | | |
|---|---|---|---|---|---|---|
| v. | Methyl Alcohol. | Mixture. | Ethyl Alcohol. | Methyl Alcohol. | Mixture. | Ethyl Alcohol. |
| 64 | 63.2 | 39.2 | 20.4 | 88.3 | 57.8 | 31.3 |
| 128 | 68.1 | 42.1 | 22.8 | 94.3 | 62.4 | 35.2 |
| 256 | 72.2 | 44.7 | 24.2 | 99.9 | 66.2 | 38.4 |
| 512 | 74.5 | 47.4 | 26.7 | 104.9 | 70.3 | 41.2 |
| 1024 | 75.9 | 50.0 | 29.2 | 108.7 | 74.2 | 44.1 |

An adequate explanation of all these facts is difficult to find. Zelinsky and Krapiwin who investigated the conductivity of aqueous methyl alcohol solutions have suggested that the cause of the low conductivity of such solutions may be due to the union of the molecules of the two solvents corresponding to certain hydrates of methyl alcohol, as $CH_3OH + 4H_2O$ or $CH_3OH + 2H_2O$. This, however, can scarcely be accepted without overwhelming evidence to support it, for we know that the

hydrate theory as applied to solutions has become a rather ingenious device, employed at times to explain almost any exceptional behavior, but as readily discarded when it does not appear to be required. With therefore practically no evidence to support it, this explanation is scarcely probable.

We have already seen that one of the theories, which has been suggested to account for the fact that electrolytes conduct only when dissolved in certain solvents, is that the dissociative power of such solvents depends on the polymerization of their molecules. Assuming that this is the true cause of such action, Jones and Lindsay have based upon it an explanation of the conductivity of electrolytes dissolved in mixed solvents. Pure water and pure alcohol have been found by the surface tension method to be associated liquids, but the molecular weight of alcohol dissolved in water is normal. Furthermore, Jones and Murray[1] have recently found that the molecular weight of any one of the three liquids, water, formic acid, or acetic acid, dissolved in any one of the remaining ones is much less than the molecular weight of the pure substance as determined by the surface tension method. This apparently shows that when two associated liquids are mixed the effect is to lower the association of one or of both of them. This being the case, it seems probable that the conductivity of an electrolyte dissolved in a mixture of two solvents in which fewer molecules are associated than in either solvent alone, would be less than the mean of the conductivities when dissolved in each solvent separately.

If the polymerization of the molecules of a solvent were really the cause of the conductivity of its solutions, this explanation would be very plausible. But it has already been shown that many substances possess conductivity when dissolved in solvents which are not polymerized at all, so that this explanation of Jones and Lindsay is not universally applicable. It would be interesting in this connection to investigate the conductivity of electrolytes dissolved in a mixture of two non-associated solvents. An adequate explanation of such phenomena as the above cannot be expected until our knowledge shall cover all possible varieties of cases of this kind.

[1] *Am. Chem. J.*, 30, 193 (1903).

# APPENDIX.

## Explanation of Tables.

The first seven tables contain the results of the most important conductivity measurements which have been published since the compilation by Kohlrausch and Holborn in 1898 in their *Leitvermögen der Elektrolyte.*

All conductivities in these tables are expressed in reciprocal ohms, except in Table IX. Concentrations are expressed in equivalents per liter, and dilutions in the number of liters in which an equivalent weight is dissolved. Where conductivity or concentration has been expressed otherwise in the original papers, the results have been recalculated.

Table I.—Conductivity of nitric acid by Veley and Manley,[1] recalculated to reciprocal ohms by the factor 1.063; conductivity of ammonia by Goldschmidt;[2] conductivity of the remainder of the electrolytes by Jones and Getman,[3] recalculated by the factor 1.066.

Table II.—Equivalent conductivities at 18° *A*, by Kohlrausch and associates[4] and, *B*, by Foster.[5] These are the most trustworthy of any conductivities thus far obtained, and they have therefore been made the basis of the values of $\Lambda_\infty$ and of migration numbers. (See Chapters VII and VIII). Numbers in parenthesis are interpolations.

Tables III and IV.—Equivalent conductivities at 0° and 95° by Kahlenberg.[6]

Tables V and VI.—Equivalent conductivities, mostly at 25°, by Jones and students.[7] In these the conductivity of the water used in preparing the solutions was subtracted in every instance. All of the numbers have been recalculated to reciprocal ohms by

1 *Phil. Mag.*, (6) **3**, 119 (1902).
2 *Physik. Zisch.*, **1**, 287 (1900).
3 *Am. Chem. J.* **27**, 443 (1902).
4 *Sitzungsber. Kgl. pr. Akad. Wiss., Berlin*, 1899, 665; 1900, 1002; 1902, 581; 1904, 1215.
5 *Phys. Rev.* **8**, 257 (1899).
6 *J. Phys. Chem.*, **5**, 348 (1901).
7 *Am. Chem. J.*, **22**, 5 and 110 (1899); **25**, 349 (1901); **26**, 428 (1901); **28**, 329 (1902).

means of the factor 1.066. Also, when it was not already the case, the conductivities have been interpolated so as to correspond to dilutions which are powers of 2.

Table VII.—Specific conductivity of saturated solutions of difficulty soluble salts at 18° by Kohlrausch.[1] The conductivity of the water employed in preparing the solutions has been deducted. Some values at other temperatures are given in the original paper.

Table VIII.—Similar results by Böttger[2] at 20°. Here also the conductivity of the water used has been subtracted.

Table IX.—Specific conductivity of pure liquids. This is not an exhaustive collection, for it has been considered to be useless to give all the values thus far obtained for those substances whose conductivity has been frequently determined, as for instance methyl and ethyl alcohols and acetone. Only the lower values have therefore in general been given. Most of the values have been expressed by the observers in mercury units, *l*, and they are so given here. Values expressed in reciprocal ohms are indicated by a *.

Table X.—Atomic weights of the more common elements.

Table XI—Equivalent weights and electrochemical equivalents, the latter based on the electrochemical equivalent of silver as found by Richards and Heimrod.[3]

Table XII.—Obach's table for use with Wheatstone bridge.

Table XIII.—Obach's logarithmic table for same purpose.

Table XIV.—Four place logarithm tables.

[1] *Ztsch. phys. Chem.* 44, 197 (1903).
[2] *Ibid.* 46, 521 (1903).
[3] *Ibid.* 41, 302 (1902).

## TABLE I.—CONDUCTIVITY OF CONCENTRATED SOLUTIONS.

### Nitric Acid, $HNO_3$, 15°.

| m. | Per cent. | κ. | Λ. |
|---|---|---|---|
| 0.208 | 1.30 | 0.064 | 308.1 |
| 0.503 | 3.12 | 0.152 | 299.2 |
| 0.981 | 5.99 | 0.270 | 275.3 |
| 1.698 | 10.13 | 0.411 | 241.4 |
| 2.646 | 15 31 | 0.535 | 202.0 |
| 3.570 | 20.11 | 0.604 | 169 3 |
| 4.766 | 25.96 | 0 625 | 131.2 |
| 5.728 | 30 43 | 0.609 | 106.4 |
| 6.499 | 33.81 | 0.592 | 91.3 |
| 6.971 | 35.90 | 0.545 | 78.2 |
| 7.815 | 39.48 | 0 530 | 67.8 |
| 9.167 | 45 01 | 0.466 | 50.9 |
| 10.90 | 51.78 | 0.378 | 34.7 |
| 11.22 | 53.03 | 0.362 | 32 3 |
| 12.59 | 58.20 | 0.297 | 23.6 |
| 13.39 | 61.20 | 0.265 | 19.8 |
| 14.63 | 65.77 | 0.206 | 14.1 |
| 15.65 | 69.53 | 0.172 | 11.0 |
| 16.82 | 73.82 | 0 115 | 6.83 |
| 17.58 | 76.99 | 0.0941 | 5.35 |
| 18.22 | 78.90 | 0.0634 | 3.48 |
| 19.66 | 84.08 | 0.0228 | 1.16 |
| 20.24 | 86.18 | 0.0202 | 1.00 |
| 20.66 | 87.72 | 0.0136 | 0.659 |
| 21.26 | 89.92 | 0.00814 | 0.383 |
| 21.79 | 91.87 | 0.00394 | 0.181 |
| 22.45 | 94.32 | 0.00168 | 0.075 |
| 22.94 | 96.12 | 0.000855 | 0.037 |
| 23.62 | 98.50 | 0.00040 | 0.017 |
| 23.74 | 98.85 | 0.00033 | 0.014 |
| 23.88 | 99.27 | 0.00043 | 0.018 |
| 24.15 | 99.97 | 0.00018 | 0.0075 |

### Ammonia, $NH_4OH$, 25°.

| m. | $10^2\kappa$. | Λ. |
|---|---|---|
| 0.0109 | 0.1220 | 11.19 |
| 0.0219 | 0.1730 | 7.90 |
| 0.0553 | 0.2718 | 4.92 |
| 0.1107 | 0.3843 | 3.47 |
| 0.3148 | 0 6339 | 2.01 |
| 0.541 | 0.7882 | 1.44 |
| 0 666 | 0.8776 | 1.32 |
| 0.817 | 0 9510 | 1.16 |
| 0.935 | 1.002 | 1.07 |
| 1.081 | 1.057 | 0.978 |
| 1.586 | 1.177 | 0.742 |
| 2.192 | 1.270 | 0.579 |
| 2.995 | 1.296 | 0.433 |
| 3.521 | 1.291 | 0.367 |
| 4.720 | 1.218 | 0.258 |
| 7 930 | 0.870 | 0.110 |
| 9.204 | 0.791 | 0.086 |
| 12.89 | 0.432 | 0.034 |

### Sulphuric Acid, $\frac{1}{2}H_2SO_4$, 0°.

| m. | κ. | Λ. |
|---|---|---|
| 2.0 | 0.2701 | 135.1 |
| 3.0 | 0.3579 | 118 0 |
| 4.0 | 0.4252 | 106.3 |
| 5.0 | 0.4765 | 95.3 |
| 6.0 | 0.4968 | 82.8 |
| 7.0 | 0.5037 | 72.0 |
| 8.0 | 0.5068 | 63.4 |
| 9.0 | 0.4805 | 53.4 |
| 10.0 | 0.4635 | 46 4 |

| | HCl, 0.° | | $HNO_3$, 0.° | | KOH, 0.° | | $NaNO_3$, 0.° | | $KNO_3$, 0.° | |
|---|---|---|---|---|---|---|---|---|---|---|
| m. | κ. | Λ. | κ. | Λ. | κ. | Λ. | κ. | Λ. | κ. | Λ. |
| 1.0 | 0.2136 | 213.6 | 0.2078 | 207.8 | 0.1208 | 120.8 | 0.0431 | 43.1 | 0.0533 | 53.3 |
| 1.2 | 0.2916 | 194.4 | 0.2557 | 197.1 | 0.1701 | 113.4 | 0.0590 | 39.3 | 0.0741 | 49.4 |
| 2.0 | 0.3628 | 181.4 | 0.3608 | 180.4 | 0.2156 | 107.8 | 0.0730 | 36.5 | | |
| 2.5 | 0.4060 | 162.4 | 0.4143 | 165.7 | 0.2595 | 103.8 | 0.0825 | 33.0 | | |
| 3.0 | 0.4539 | 151.3 | 0.4509 | 150.3 | | | | | | |

| | ½CaCl₂, 0.° | | ½SrCl₂, 0.° | | ½BaCl₂, 0.° | |
|---|---|---|---|---|---|---|
| m. | κ. | Λ. | κ. | Λ. | κ. | Λ. |
| 1.0 | | | 0.0449 | 44.9 | 0.1 | 0.0062 | 61.9 |
| 2.0 | 0.0759 | 38.0 | 0.0795 | 39.8 | 0.2 | 0.0111 | 55.3 |
| 3.0 | 0.0993 | 33.1 | 0.1008 | 33.6 | 0.5 | 0.0256 | 51.2 |
| 4.0 | 0.1152 | 28.8 | 0.1178 | 29.5 | 1.0 | 0.0476 | 47.6 |
| 5.0 | 0.1250 | 25.0 | | | 1.5 | 0.0682 | 45.5 |

## TABLE II.—EQUIVALENT CONDUCTIVITY OF ELECTROLYTES AT 18°.

| (Λ) m. | KCl. | KBr. | KI. | $KNO_3$. | KSCN. | $KClO_3$. | KF. | $KIO_3$. | v. |
|---|---|---|---|---|---|---|---|---|---|
| 0.0001 | 139.05 | 131.15 | 139.76 | 125 49 | 130.22 | 118.63 | 110.47 | 97.64 | 10000 |
| 0.0002 | 128.76 | 130.86 | 129.50 | 125.18 | 120.02 | 118.35 | 110.22 | 97.34 | 5000 |
| 0.0005 | 128.09 | 130.15 | 128.97 | 124.44 | 119.38 | 117.68 | 109.57 | 96.72 | 2000 |
| 0.001 | 127.33 | 129.38 | 128.25 | 123.64 | 118.64 | 116.92 | 108.89 | 96.04 | 1000 |
| 0.002 | 126.29 | 128.32 | 127.21 | 122.59 | 117.65 | 115.84 | 107.91 | 95.04 | 500 |
| 0.005 | 124.40 | 126.40 | 125.33 | 120.47 | 115 81 | 113.84 | 106.16 | 93.19 | 200 |
| 0.01 | 122.42 | 124.40 | 123.44 | 118.20 | 113.95 | 111.64 | 104.28 | 91.24 | 100 |
| 0 02 | 120.00 | 121.87 | 121.10 | 115.27 | 111.59 | 108.81 | 101.87 | 88.64 | 50 |
| 0.05 | 115.94 | 117.78 | 117.26 | 110.09 | 107.74 | 103.74 | 97.73 | 84.00 | 20 |
| 0.1 | 112.00. | 114.22 | 113.98 | 104.77 | 104.28 | 99.19 | 94.02 | 79.67 | 10 |
| 0.2 | 107.96 | 110.40 | (110.50) | 98.74 | (100.70) | 93.73 | (89.95) | 74.34 | 5 |
| 0.5 | 102.40 | 105.37 | 106.20 | 89.23 | 95.69 | 85.28 | 82.60 | . . | 2 |
| 1.0 | 98.28 | . . | 103.60 | 80.47 | 91.61 | . . | 76.00 | . . | 1 |

TABLE II.—(*Continued*).

| *m*. | NaCl. | $NaNO_3$. | NaF. | $NaIO_3$. | LiCl. | $LiNO_3$. | $LiIO_3$. | RbCl. | *v*. |
|---|---|---|---|---|---|---|---|---|---|
| 0.0001 | 108.06 | 104.53 | 89.35 | 76.69 | 98.06 | 94.38 | 66.66 | 132.3 | 10000 |
| 0.0002 | 107 80 | 104.18 | 89.06 | 76.44 | 97.78 | 94.07 | 66.43 | . . | 5000 |
| 0.0005 | 107.18 | 103.53 | 88.49 | 75.83 | 97.13 | 93.45 | 65.87 | . . | 2000 |
| 0.001 | 106.48 | 102.85 | 87.86 | 75.19 | 96.45 | 92.80 | 65.27 | 130.3 | 1000 |
| 0 002 | 105.55 | 101.88 | 86.99 | 74.30 | 55.55 | 91.91 | 64 43 | . . | 500 |
| 0.005 | 103.79 | 100.07 | 85 27 | 72.62 | 93.86 | 90.27 | 62.89 | . . | 200 |
| 0 01 | 101.95 | 98.16 | 83.48 | 70.86 | 92 08 | 88.55 | 61.23 | 125.3 | 100 |
| 0.02 | 99 66 | 95.70 | 81.1 | 68.56 | 89.88 | 86.38 | 59.05 | . . | 50 |
| 0.05 | 95.86 | 91.60 | 77.03 | 64.43 | 86.22 | 82.56 | 55.26 | . . | 20 |
| 0 1 | 92.01 | 87.24 | 73.14 | 60.46 | 82.35 | 79.24 | 51.50 | 113.9 | 10 |
| 0.2 | 87.73 | 82.28 | 68.0 | 55.45 | 77.93 | 75.06 | 46.88 | . . | 5 |
| 0.5 | 80.93 | 74.05 | 60.0 | . . | 70.65 | 68.03 | 38.98 | . . | 2 |
| 1.0 | 74.34 | 65.86 | 51.9 | . . | 63 30 | 60.80 | 31.21 | 101.9 | 1 |

| *m*. | CsCl. | $AgNO_3$. | TlCl. | $TlNO_3$. | TlP. | $NH_4NO_3$. | NaOH. | | *v*. |
|---|---|---|---|---|---|---|---|---|---|
| 0 0001 | 132.3 | 115.01 | 130.33 | 126.63 | 114.38 | 126.1 | . . | | 10000 |
| 0.0002 | 132.0 | 114.56 | 130.00 | 126 30 | 114.64 | 126.0 | . . | | 5000 |
| 0.0005 | 131.38 | 113.88 | 129.18 | 125.61 | 114.45 | (125 3) | . . | | 2000 |
| 0.001 | 130.68 | 113.14 | 128.23 | 124.70 | 113.25 | 124.5 | . . | | 1000 |
| 0.002 | 129.52 | 112.07 | 126 81 | 123.48 | 111.29 | 123.0 | 204.5 | | 500 |
| 0.005 | 127.47 | 110.03 | 123.73 | 121.11 | 108.18 | (120.3) | (204.3) | | 200 |
| 0.01 | 125.20 | 107.80 | 120.21 | 118.38 | 105.44 | 118.0 | 203.4 | | 100 |
| 0.02 | (122.15) | (104.55) | . . | (114.40) | 102.22 | (114.6) | (202.0) | | 50 |
| 0.05 | (117.70) | 99.50 | . . | 107.93 | 97.38 | 110 0 | 199 0 | | 20 |
| 0 01 | 113.35 | 94.33 | . . | 101. 19 | 92.61 | 105.6 | 195.4 | | 10 |
| 0.02 | . . | (87.5) | . . | . . | (87.00) | (102.3) | (187.5) | | 5 |
| 0.5 | . . | 77.3 | . . | . . | 78.78 | 94.5 | 174.1 | | 2 |
| 1.0 | . . | 67.6 | . . | . . | 71.54 | 88.8 | 157.0 | | 1 |

| *m*. | ½ $BaCl_2$. | ½ $Ba(NO_3)_2$. | ½ $Sr(NO_3)_2$. | ½ $CaCl_2$. | ½ $Ca(NO_3)_2$. | ½ $MgCl_2$. | ½ $Pb(NO_3)_2$. | ½ $K_2SO_4$. | *v*. |
|---|---|---|---|---|---|---|---|---|---|
| 0.0001 | | 115.32 | 111.74 | 115.17 | 111.91 | 109.43 | 120.73 | 130.76 | 10000 |
| 0.0002 | | 114.65 | 111.07 | 114.55 | 111.19 | 108.87 | 119 94 | 130.08 | 5000 |
| 0.0005 | 117 01 | 113.30 | 109.76 | 113.34 | 109 93 | 107.68 | 118.08 | 128.57 | 2000 |
| 0.001 | 115.60 | 111.72 | 108.31 | 111.96 | 108.49 | 106.35 | 116.13 | 126.93 | 1000 |
| 0.002 | (113.67) | 109 50 | 106.35 | 110.07 | 106.54 | 104.52 | 113.54 | (124.63) | 500 |
| 0.005 | (110.12) | 105.29 | 102.74 | 106 70 | 103.07 | 101.30 | 108 68 | 120.29 | 200 |
| 0.01 | 106.67 | 100.96 | 99.04 | 103.37 | 99.53 | 98.14 | 103.55 | 115.84 | 100 |
| 0.02 | 102.53 | 95.66 | 94.52 | 99.38 | 95.18 | 94.33 | 97.01 | 110.38 | 50 |
| 0.05 | 96.04 | 86.81 | 87.30 | 93.29 | 88 41 | 88.47 | 86.38 | 101.93 | 20 |
| 0.1 | 90.78 | 78 94 | 80 93 | 88.19 | 82.48 | 83.42 | 77.27 | 94.91 | 10 |
| 0.2 | 85.18 | 70.18 | 73 80 | 82.79 | 75.94 | 77.84 | 67.36 | 87.76 | 5 |
| 0 5 | 77.29 | 56.60 | 62.72 | 74.92 | 65.70 | 69 50 | 53.41 | 78.43 | 2 |
| 1.0 | 70.14 | | 52.07 | 67.54 | 55.86 | 61 45 | 42.02 | 71.59 | 1 |

| *m*. | ½ $Li_2SO_4$. | ½ $K_2C_2O_4$. | ½ $MgSO_4$. | ½ $ZnSO_4$. | ½ $CdSO_4$. | ½ $CuSO_4$. | ½ $CaCrO_4$. | ½ $MgC_2O_4$.(?) | *v*. |
|---|---|---|---|---|---|---|---|---|---|
| 0.0001 | . . | 125.16 | 109.90 | 109.53 | 109.84 | 109.95 | 126.2 | 94.5 | 10000 |
| 0.0002 | . . | 124.90 | 108.07 | 107.46 | 107.60 | 107.90 | 109.4 | 87.0 | 5000 |
| 0.0005 | 97.86 | 123.89 | 104.21 | 103.16 | 102.93 | 103.56 | 109.5 | 74.5 | 2000 |
| 0.001 | 96.42 | 122.52 | 99.89 | 98.39 | 97 72 | 58.56 | 106 9 | 63.4 | 1000 |
| 0.002 | (94.40) | 120.53 | 94.14 | 92.05 | 90.92 | 91.94 | 102.1 | 51.4 | 500 |
| 0.005 | (90.67) | 116.80 | 84.53 | 81.76 | 79.70 | 80.98 | 93.12 | 38.2 | 200 |
| 0.01 | 86.85 | 112.89 | 76.21 | 72.76 | 70.34 | 71.74 | 85 03 | 29.6 | 100 |
| 0.02 | 82.18 | 108.13 | 67.68 | 63.73 | 60.95 | 62.40 | 76.56 | 23.0 | 50 |
| 0.05 | 74.69 | 100.83 | 56.92 | 52.68 | 49.60 | 51.16 | 65.93 | 16.4 | 20 |
| 0 1 | 68.16 | 94.84 | 49.68 | 45.34 | 42.21 | 43.85 | 58.77 | 12.7 | 10 |
| 0.2 | 61.05 | 88.62 | 43.19 | 39.08 | 35.89 | 37.66 | 52.53 | 10.0 | 5 |
| 0.5 | 50.52 | . . | . . | . . | 28.74 | . . | 43.03 | . . | 2 |
| 1.0 | 41.35 | 73.66 | 28.91 | 26.21 | 23.58 | 25.77 | 32.98 | . . | 1 |

| (*B*). *m*. | ½ $MgCl_2$. | ½ $MgSO_4$. | ½ $C_2O_4H_2$. | ½ $C_4O_6H_2$. | $NaNH_4HPO_4$. | $Na_2HPO_4$. | $KH_2PO_4$. | $K_2HPO_4$. | *v*. |
|---|---|---|---|---|---|---|---|---|---|
| 0.0001 | 115.1 | 111.4 | 235.2 | 136.8 | . . | . . | . . | . . | 10000 |
| 0.0002 | 113.5 | 109.1 | 224.5 | 122.1 | . . | . . | . . | . . | 5000 |
| 0 0005 | (111.3) | (104.1) | (199.3) | (103.0) | . . | . . | . . | . . | 2000 |
| 0.001 | 109 7 | 100.0 | 180.7 | 88.4 | . . | 58.4 | 31.7 | 105.0 | 1000 |
| 0.002 | 107.9 | 93.8 | 172.1 | 74.0 | 62.2 | 57.7 | 31.2 | 102.8 | 500 |
| 0.005 | (104.8) | (84.5) | (164.1) | (55.1) | (60.6) | (56.1) | (30.4) | (95.1) | 200 |
| 0.01 | 101.4 | 76 1 | 158.2 | 42.5 | 58.4 | 54.0 | 29.5 | 85.0 | 100 |
| 0.02 | (96.1) | (67.8) | (149.3) | (32.4) | (56.0) | (51.8) | (28 7) | (73.9) | 50 |
| 0.05 | 89.8 | 56.6 | 132.9 | 22.0 | 51.4 | 48.0 | 27.8 | 58.5 | 20 |
| 0.1 | 84.7 | 49.5 | 116 9 | 16 1 | 47.5 | 44.0 | 26.7 | 46.8 | 10 |
| 0.2 | (80 3) | (43.0) | (99.5) | (11.9) | (42.7) | (39.7) | (25.3) | (38.7) | 5 |
| 0.5 | 75.5 | 35.2 | 80.0 | 7.1 | 36.1 | 33.4 | 23.2 | 29.1 | 2 |

TABLE III.—EQUIVALENT CONDUCTIVITY OF ELECTROLYTES AT 0°

| v. | NaCl. | KCl. | KI. | ½ $BaCl_2$. | $KClO_3$. | $NaNO_3$. | $KNO_3$. | $AgNO_3$. | ½ $Ba(NO_3)_2$. | ½ $Sr(NO_3)_2$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 0.25 | 31.0 | . . | . . | . . | . . | 24.5 | . . | 27.2 | . . | . . |
| 0.5 | 41.8 | 63.9 | 69.3 | 38.7 | . . | 34.7 | . . | 35.3 | . . | 23.5 |
| 1.0 | 47.4 | 65.6 | 69.5 | 44.0 | . . | 46.5 | 52.1 | 44.5 | . . | 32.1 |
| 2.0 | 50.8 | 67.3 | 69.7 | 47.0 | . . | 48.0 | 56.5 | 48.3 | . . | 36.4 |
| 4.0 | 53.3 | 69.0 | 69.9 | 50.6 | 55.4 | 49.0 | 60.6 | 53.3 | 41.9 | 43.2 |
| 8.0 | 55.7 | 70.6 | 71.5 | 53.8 | 60.2 | 52.8 | 63.8 | 57.8 | 45.6 | 47.8 |
| 16.0 | 57.9 | 73.0 | 73.5 | 57.0 | 63.2 | 55.7 | 66.6 | 60.1 | 50.4 | 51.3 |
| 32.0 | 59.5 | 75.0 | 76.5 | 60.0 | 65.6 | 57.6 | 70.2 | 63.7 | 55.2 | 55.5 |
| 64.0 | 60.9 | 76.6 | 77.7 | 63.5 | 67.7 | 59.7 | 72.7 | 66.6 | 59 3 | 58 4 |
| 128.0 | 62 3 | 77.7 | 78.9 | 65.9 | 69.0 | 61.1 | 73.9 | 67.8 | 62.6 | 61.0 |
| 256.0 | 64.2 | 78.9 | 79.4 | 71.0 | 70.3 | 62.3 | 75.5 | 68.8 | 64.9 | 63.1 |
| 512.0 | 65.3 | 79 6 | 79.8 | 72.3 | 71.5 | 63.5 | 75.9 | 69.7 | 66.7 | 64.5 |
| 1024.0 | 67.7 | 80.5 | 80.7 | . . | 72.1 | 64.3 | 76.8 | 70.2 | 67.9 | 66.1 |
| 2048.0 | 67.8 | 80.9 | . . | . . | 72.5 | 65.2 | 77.7 | 70.7 | 68.0 | 67.9 |
| 4096.0 | 67.7 | . . | . . | . . | . . | . . | 78.4 | 70.5 | . . | 68.0 |

| v. | ½ $K_2SO_4$. | ½ $MgSO_4$. | ½ $ZnSO_4$. | ½ $MnSO_4$. | ½ $CdSO_4$. | ½ $NiSO_4$. | ½ $CoSO_4$. | ½ $FeSO_4$. | ½ $CuSO_4$. |
|---|---|---|---|---|---|---|---|---|---|
| 0.25 | . . | 7.0 | 7.1 | . . | 6.7 | . . | . . | . . | . . |
| 0.5 | . . | 13.0 | 12.6 | 12.1 | 11.4 | 13.1 | . . | 12.1 | 12.3 |
| 1.0 | . . | 17.6 | 16.3 | 15.8 | 15.0 | 17.8 | 15.5 | 16.3 | 15.9 |
| 2.0 | 48.4 | 21.2 | 21.7 | 19.2 | 18.3 | 21.6 | 18.7 | 19.6 | 19.0 |
| 4.0 | 52.6 | 25.2 | 24.7 | 23.4 | 21.3 | 25.3 | 22.0 | 23.0 | 22 4 |
| 8.8 | 56.7 | 29.5 | 28.3 | 26.1 | 25.0 | 28.9 | 25.7 | 28.1 | 26.2 |
| 16.0 | 61.8 | 33.7 | 32.2 | 31.2 | 29.5 | 33.9 | 30.2 | 31.4 | 31.0 |
| 32.0 | 65.2 | 38.7 | 37.0 | 35.8 | 34.3 | 39.0 | 34.7 | 36.3 | 35.9 |
| 64.0 | 68.8 | 43.3 | 41.9 | 41.0 | 40.3 | 44.8 | 40.0 | 41.7 | 41.2 |
| 128.0 | 71.5 | 47.9 | 47.5 | 46.3 | 45.6 | 50.8 | 45 6 | 47.2 | 46.8 |
| 256.0 | 74.8 | 52.7 | 52.9 | 51.4 | 50.5 | 56.0 | 50.6 | 52.1 | 51.9 |
| 512.0 | 75.6 | 56.6 | 56 8 | 56.3 | 56.2 | 59.6 | 55.2 | 56.0 | 56.3 |
| 1024.0 | 76.9 | 60.5 | 61.0 | 59.4 | 59.4 | 63.0 | 58.4 | 59.5 | 60.7 |
| 2048.0 | 78.0 | 63.6 | 64.4 | 62.8 | 62.4 | 64.6 | 61.7 | 62.0 | 63.2 |
| 4096.0 | 79.0 | 66.2 | 65.4 | 65.6 | 63.4 | 65.9 | 64.3 | 63.4 | 66.4 |
| 8192.0 | . . | 67.8 | 65.9 | 65.5 | . . | . . | 64.7 | 64.9 | 67.3 |

TABLE IV.—EQUIVALENT CONDUCTIVITY OF ELECTROLYTES AT 25°.

| v. | NaCl. | KCl. | KBr. | KI. | ½ $MgCl_2$. | ½ $BaCl_2$. | ½ $HgCl_2$ | $KClO_3$. | $KNO_3$. |
|---|---|---|---|---|---|---|---|---|---|
| 0.25 | 115.9 | 169.1 | 121.9 | 114.3 | . . | . . | . . | . . | . . |
| 0.5 | 156.1 | 213.2 | 222.8 | 216.3 | . . | . . | . . | . . | . . |
| 1.0 | 206.7 | 261.0 | 245.4 | 252.8 | 158.7 | 146.3 | . . | 185.9 | 198.1 |
| 2.0 | 215.5 | 271.9 | 265.3 | 261.7 | 183.4 | 171.1 | 1.93 | 208.3 | 216.6 |
| 4.0 | 236.3 | 284.8 | 286 0 | 274.3 | 197.5 | 193.9 | 2.12 | 235.6 | 251.3 |
| 8.0 | 267.5 | 289.5 | 296.4 | 296.3 | 222.6 | 218.5 | 3.98 | 248.7 | 269.4 |
| 16.0 | 271.5 | 313.2 | 317.7 | 305.4 | 255.1 | 240.4 | 5.24 | 266.2 | 288.2 |
| 32.0 | 277.2 | 334.4 | 325.8 | 315.1 | 257.7 | 276.1 | 8.78 | 284.1 | 304.6 |
| 64.0 | 288.0 | 360.3 | 338.1 | 331.6 | 272.1 | 297.1 | 14.4 | 300.0 | 320.4 |
| 128.0 | 302.6 | 363.9 | 340.4 | 341.4 | 278.6 | 308.1 | 18.6 | 310.3 | 323.1 |
| 256.0 | 310.0 | 373.5 | 343.9 | 348.2 | 285.2 | 326.0 | 28 8 | 320.8 | 330.1 |
| 512.0 | 318.8 | 401.8 | 351.5 | 357.5 | 290.9 | 338.9 | 45.9 | 327.7 | 338.7 |
| 1024.0 | 328.3 | 419.8 | 360.5 | 368.2 | 319.3 | 352.8 | 77.1 | 333.6 | 349.9 |
| 2048.0 | 339.1 | 433.3 | 375.0 | 389.8 | 317.1 | 363.1 | 106.2 | 337.9 | 349.6 |

| v. | $AgNO_3$. | ½ $MgSO_4$. | ½ $ZnSO_4$. | ½ $MnSO_4$. | ½ $CdSO_4$. | ½ $NiSO_4$. | ½ $CoSO_4$. | ½ $FeSO_4$. | ½ $CuSO_4$. |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 180.5 | 75.6 | 64.2 | 58.2 | 52.5 | 70.8 | 64.8 | 60.6 | 58.8 |
| 2 | 205.0 | 91.1 | 76.7 | 70.0 | 63.6 | 84 5 | 74.7 | 74.3 | 87.9 |
| 4 | 228.7 | 103.7 | 87.8 | 84 7 | 74 6 | 98.7 | 87.8 | 89.2 | 76.8 |
| 8 | 244.4 | 121.0 | 104.0 | 100.4 | 88.6 | 114 2 | 107.8 | 103 5 | 92.2 |
| 16 | 252.4 | 142 7 | 123.2 | 119.6 | 109.7 | 133.4 | 123.9 | 125.5 | 108.7 |
| 32 | 266.8 | 169.7 | 149.4 | 141.4 | 131.2 | 157.7 | 144.7 | 144.2 | 133.8 |
| 64 | 293.7 | 191.7 | 172.0 | 171.2 | 152.2 | 183.2 | 178 0 | 173.0 | 150.5 |
| 128 | 303.0 | 227.4 | 202.9 | 197.3 | 185 6 | 213.0 | 209.6 | 211.5 | 180.8 |
| 256 | 309.0 | 259.6 | 232 1 | 236.4 | 225.1 | 253.4 | 241.0 | 250.3 | 218.9 |
| 512 | 319.3 | 295.4 | 257.4 | 275 4 | 261.7 | 298 6 | 282.7 | 275.9 | 246.8 |
| 1024 | 322.3 | 335.4 | 268.4 | 309 8 | 300.2 | 316.8 | 321 2 | 319.9 | 275.9 |
| 2048 | 343.4 | 387.6 | 277.6 | 338.6 | 357.0 | 359 6 | 383.4 | 413.1 | 298.3 |

TABLE V.—EQUIVALENT CONDUCTIVITY OF ELECTROLYTES AT TEMPERATURES 0° TO 35°.

Hydrochloric Acid, HCl.

| v. | 0°. | 15°. | 25°. | 35°. |
|---|---|---|---|---|
| 2 | 230.8 | 305.4 | 353.6 | 396.2 |
| 8 | 243.3 | 327.5 | 380 2 | 431.9 |
| 16 | 245.9 | 330.5 | 388.5 | 442.6 |
| 32 | 249.0 | 342.3 | 395.6 | 448.4 |
| 128 | 254.8 | 349.1 | 403.7 | 458.8 |
| 512 | 256.4 | 349.3 | 403.7 | 458.8 |
| 1024 | 256.5 | 349.3 | 403.7 | 458.8 |
| 2048 | 256.3 | 348.9 | 403.0 | 458.8 |

Nitric Acid $HNO_3$.

| 0°. | 13°. | 25°. | 35°. |
|---|---|---|---|
| 227.4 | 288.9 | 344.8 | 394.9 |
| 239.2 | 311.3 | 373.6 | 427.0 |
| 246.7 | 319 1 | 383.8 | 437.6 |
| 247.3 | 323 2 | 389.1 | 445.7 |
| 250.0 | 327.2 | 389.5 | 449.2 |
| 251.2 | 327.2 | 390.5 | 448.6 |
| 251.2 | 327.3 | 392.3 | 449.2 |
| 251.2 | 327.3 | 392.3 | 449.2 |

Sulphuric Acid, $\frac{1}{2}H_2SO_4$

| v | 0° | 15° | 25° | 35° |
|---|---|---|---|---|
| 1 | 147.8 | 184.4 | 207.9 | 247.3 |
| 4 | 163.2 | 208.4 | 227.0 | 261.2 |
| 8 | 172.0 | 218.5 | 239.7 | 285.2 |
| 16 | 187.0 | 237.4 | 261.2 | 314.8 |
| 64 | 213.6 | 278.9 | 310.6 | 365.0 |
| 256 | 239 8 | 304.7 | 359 8 | 405.1 |
| 512 | 253.2 | 335.8 | 371.5 | 448.8 |
| 1024 | 260.3 | 343 0 | 376.2 | 454.7 |
| 2048 | 262.3 | 346.5 | 380.0 | 455.2 |
| 4096 | 263.9 | 346.5 | 380.0 | 456.3 |
| 8192 | 266.5 | 346.5 | 380.0 | 456.3 |

Potassium Hydroxide, KOH

| v | 0° | 18° | 25° | 35° |
|---|---|---|---|---|
| 1 | 121.0 | 183.2 | 197.4 | 229.0 |
| 2 | 126.2 | 196.2 | 211.0 | 242.8 |
| 8 | 130.9 | 206 8 | 214.8 | 247.5 |
| 16 | 133.6 | 213.2 | 226 0 | 263 8 |
| 32 | 136.0 | 218.6 | 237.7 | 272.9 |
| 128 | 142.5 | 226.4 | 240 9 | 274.7 |
| 256 | 142.9 | 228.2 | 240.9 | 275.0 |
| 512 | 142.9 | 228.2 | 240.9 | 275.0 |

Sodium Hydroxide, NaOH

| 0° | 18° | 25° | 35° |
|---|---|---|---|
| 103.9 | 156.7 | 173.3 | 201.9 |
| 111.2 | 173 8 | 188.7 | 220.1 |
| 122.6 | 181.2 | 207.9 | 243.8 |
| 124.7 | 185.5 | 213.4 | 248.2 |
| 129.4 | 191.9 | 218.9 | 250.0 |
| 132.2 | 199.3 | 226.0 | 260.9 |
| 133.3 | 200 4 | 226.0 | 258.0 |
| 133.3 | 200.4 | 223.9 | 255 8 |

Potassium Chloride, KCl

| v | 0° | 7.1° | 25° | 35° |
|---|---|---|---|---|
| 1 | 62.4 | 77.2 | 109.8 | 129.4 |
| 2 | 66.1 | 79.5 | 115.1 | 137.5 |
| 8 | 71.1 | 81 0 | 126.5 | 150.7 |
| 16 | 74.6 | 89.3 | 130.7 | 157 2 |
| 32 | 76.8 | 93.8 | 136.9 | 161.0 |
| 128 | 80.0 | 97.0 | 143.8 | 175.2 |
| 512 | . . | . . | . . | . . |
| 1024 | 83.1 | 101.3 | 149.0 | 180.2 |
| 2048 | 84.0 | 101.3 | 148.4 | 180.2 |

Potassium Bromide, KBr.

| 0° | 18° | 25° | 35° |
|---|---|---|---|
| . . | . . | . . | . . |
| 70.8 | 105.7 | 120.7 | 138.0 |
| 73.9 | 113.1 | 128.3 | 151.6 |
| 78.2 | 117.4 | 133.9 | 159.2 |
| 80.1 | 122.7 | 137.5 | 163.3 |
| 82.6 | 128.0 | 146.0 | 171.0 |
| 85.2 | 131.1 | 150.3 | 181.9 |
| 89.8 | 133.2 | 152.9 | 184.6 |
| 89.8 | 133.2 | 152.9 | 184.6 |

Potassium Iodide, KI

| v | 0° | 18° | 25° | 35° |
|---|---|---|---|---|
| 1 | 63.7 | 100.2 | 115.2 | 134.9 |
| 2 | 66.5 | 105.3 | 118.9 | 140.7 |
| 8 | 70.7 | 110.9 | 128.0 | 151.7 |
| 16 | 75.3 | 114.3 | 131.0 | 156.5 |
| 32 | 77.7 | 121.2 | 137.4 | 165.2 |
| 128 | 81.4 | 124.0 | 143.9 | 170.1 |
| 512 | 83.1 | 126.9 | 149.2 | 177.0 |
| 1024 | 83.1 | 126.8 | 150.3 | 177.0 |
| 2048 | 83.1 | 129.0 | 150.3 | 177.7 |

Potassium Nitrate, $KNO_3$

| 0° | 7.5° | 25° | 35° |
|---|---|---|---|
| 54.2 | 65.6 | 94.9 | 106.7 |
| 56.7 | 69.1 | 101.2 | 120.9 |
| 64.1 | 79.9 | 114.1 | 136.8 |
| 69.3 | 86.6 | 124.0 | 149.3 |
| 74.9 | 88.3 | 128.8 | 153.5 |
| 76.3 | 92.4 | 136.5 | 165.5 |
| 76.7 | 99.1 | 139.6 | 167.9 |
| 78.5 | 99.1 | 139.4 | 167.8 |
| 78.5 | 99.1 | 139.6 | 168.4 |

Sodium Nitrate. $NaNO_3$.

| v. | 0°. | 13°. | 25°. | 35°. |
|---|---|---|---|---|
| 1 | 43.0 | 59.6 | 75.0 | 89.3 |
| 2 | 47.9 | 67.1 | 83.9 | 100.8 |
| 4 | . . | . . | . . | . . |
| 8 | 53.8 | 75.7 | 97.0 | 116.0 |
| 16 | 57.1 | 79 9 | 103.8 | 124.2 |
| 32 | 62.0 | 84.2 | 108.4 | 130.4 |
| 64 | . . | . . | . . | . . |
| 128 | 65.9 | 90.6 | 115.8 | 138.8 |
| 256 | . . | . . | . . | . . |
| 512 | 67.8 | 92.7 | 118.9 | 144.8 |
| 1024 | 68.2 | 96.5 | 121.2 | 146.5 |
| 2048 | 69.0 | 96.9 | 121.2 | 147.1 |

Ammonium Nitrate, $NH_4NO_3$.

| 0°. | 9°. | 25°. | 35°. |
|---|---|---|---|
| 58.9 | 71.8 | 100.1 | 119.0 |
| 62.1 | 78.0 | 107.7 | 128.0 |
| 65.2 | 82.8 | 114.1 | 136.2 |
| 67.7 | 86.9 | 120.0 | 144.1 |
| 71.0 | 90.8 | 125.8 | 150.5 |
| 73.5 | 93.3 | 130.1 | 156.4 |
| 75.4 | 95.1 | 133.2 | 161.0 |
| 77.0 | 97.1 | 136.4 | 164.2 |
| 79.2 | 100.0 | 139.5 | 170.1 |
| 80.7 | 103.3 | 142.6 | 177.2 |
| 82.0 | 106.3 | 145.5 | 183.5 |
| 83.2 | 105.6 | 147.0 | 182.2 |

TABLE V.—(*Continued.*)

| | Potassium Permanganate, $KMnO_4$. | | | | Potassium Sulphate, $\frac{1}{2}K_2SO_4$. | | | |
|---|---|---|---|---|---|---|---|---|
| v. | 0°. | 10.3°. | 25°. | 35°. | 0°. | 18°. | 25°. | 35°. |
| 1 | . . | . . | . . | . . | 46.3 | 71.1 | 80.3 | 93.7 |
| 4 | . . | . . | . . | . . | 55.4 | 85.3 | 96.9 | 116.5 |
| 8 | 61.2 | 82.8 | 113.8 | 134.5 | 60.5 | 93.1 | 104.6 | 125.6 |
| 16 | 66.3 | 86.7 | 117.0 | 141.0 | 65.4 | 97.5 | 110.4 | 135.8 |
| 32 | 69.3 | 90.0 | 120.3 | 145.8 | . . | . . | . . | . . |
| 64 | 71.0 | 92.7 | 123.4 | 149.0 | 73.8 | 112.2 | 131.4 | 157.1 |
| 128 | 71.9 | 94.4 | 126.7 | 152.4 | . . | . . | . . | . . |
| 256 | 72.8 | 95.6 | 129.0 | 155.0 | 78.9 | 123.6 | 141.9 | 167.0 |
| 512 | 73.0 | 95.8 | 129.0 | 155.4 | 84.2 | 130.9 | 146.3 | 173.9 |
| 1024 | 73.2 | 95.9 | 129.0 | 155.6 | 85.4 | 131.8 | 147.1 | 175.9 |
| 2048 | 72.5 | 94.9 | 129.0 | 153.5 | 85.4 | 131.8 | 147.1 | 175.9 |

| | Lithium Nitrate, $LiNO_3$. | | Strontium Iodide, $\frac{1}{2}SrI_2$. | |
|---|---|---|---|---|
| v. | 0°. | 25°. | 0°. | 25°. |
| 16 | . . | . . | 60.3 | 109.4 |
| 32 | 53.3 | 97.9 | 62.7 | 114.3 |
| 64 | 54.9 | 100.9 | 65.1 | 118.9 |
| 128 | 56.0 | 104.5 | 67.2 | 123.5 |
| 256 | 56.9 | 106.3 | 69.2 | 128.0 |
| 512 | 58.3 | 108.0 | 70.7 | 130.6 |
| 1024 | 59.0 | 109.0 | . . | . . |

TABLE VI.—EQUIVALENT CONDUCTIVITY OF ELECTROLYTES AT 25°.

| v. | NaBr. | $NH_4Cl$. | $NH_4Br$. | KCN. | $\frac{1}{2}CaCl_2$. | $\frac{1}{2}CaBr_2$. | $\frac{1}{2}SrCl_2$. |
|---|---|---|---|---|---|---|---|
| 1 | 85.6 | 105.8 | 107.3 | 121.8 | 71.8 | 79.3 | 69.3 |
| 2 | 93.8 | 111.8 | 113.4 | 130.6 | 81.2 | 88.7 | 78.1 |
| 4 | 100.6 | 117.7 | 119.6 | 136.9 | 90.3 | 97.1 | 86.7 |
| 8 | 107.4 | 123.4 | 125.7 | 142.7 | 97.9 | 104.2 | 93.7 |
| 16 | 112.3 | 128.8 | 130.4 | 148.3 | 105.0 | 110.0 | 103.5 |
| 32 | 116.7 | 134.2 | 135.4 | . . | 112.3 | 115.8 | 109.2 |
| 64 | 120.2 | 139.1 | 139.1 | . . | 118.5 | 121.5 | 114.9 |
| 128 | 123.5 | 142.4 | 142.3 | . . | 125.0 | 127.2 | 120.5 |
| 256 | 126.2 | 144.2 | 145.7 | . . | 130.5 | 131.6 | 125.2 |
| 512 | 128.2 | 146.2 | 148.0 | . . | 131.5 | 135.4 | 129.3 |
| 1024 | 129.0 | 147.7 | 149.9 | . . | 133.0 | 139.0 | 132.8 |
| 2048 | 129.2 | 148.4 | 151.3 | . . | 141.6 | 143.2 | 136.0 |

| v. | $\frac{1}{2}SrBr_2$. | $\frac{1}{2}BeCl_2$. | $\frac{1}{2}BeBr_2$. | $\frac{1}{2}MgCl_2$. | $\frac{1}{2}MgBr_2$. | $\frac{1}{2}CdCl_2$. | $\frac{1}{2}CdBr_2$. |
|---|---|---|---|---|---|---|---|
| 1 | 73.9 | 70.1 | 78.7 | 69.2 | 82.0 | 24.8 | 19.4 |
| 2 | 85.6 | 79.1 | 86.6 | 78.0 | 90.0 | 31.7 | 27.3 |
| 4 | 94.2 | 88.6 | 94.1 | 86.7 | 97.8 | 44.8 | 36.9 |
| 8 | 101.0 | 99.0 | 101.8 | 94.2 | 102.0 | 55.0 | 47.1 |
| 16 | 110.9 | 107.3 | 107.7 | 100.6 | 109.8 | 66.7 | 57.5 |
| 32 | 118.0 | 113.7 | 114.5 | 106.7 | 115.4 | 77.0 | 68.9 |
| 64 | 123.3 | 119.8 | 120.2 | 111.8 | 120.8 | 88.1 | 80.5 |
| 128 | 130.3 | 127.0 | 126.3 | 117.3 | 125.1 | 98.3 | 92.4 |
| 256 | 135.4 | 132.3 | 131.5 | 121.0 | 130.5 | 106.8 | 104.0 |
| 512 | 139.4 | 138.7 | 135.6 | 124.0 | 135.2 | 114.9 | 115.0 |
| 1024 | 145.1 | 143.8 | 140.8 | 127.8 | 137.3 | 124.0 | 124.2 |
| 2048 | 150.4 | 147.0 | 146.3 | 132.7 | . . | . . | . . |

| v | $\frac{1}{2}(NH_4)_2SO_4$ | $\frac{1}{2}MgSO_4$ | $\frac{1}{2}CuSO_4$ | $\frac{1}{2}CdSO_4$ | $\frac{1}{2}NiSO_4$ | $\frac{1}{2}FeSO_4$ | $\frac{1}{2}AlCl_3$ | $\frac{1}{2}HgCl_2$ | $\frac{1}{2}Hg(CN)_2$ |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 77.9 | 33.4 | 29.7 | 26.3 | . . | 32.7 | 60.9 | 0.38 | . . |
| 2 | 87.0 | 40.9 | 35.5 | 32.2 | . . | . . | 70.5 | 0.56 | 0.16 |
| 4 | 95.3 | 47.5 | 39.7 | 38.7 | 41.5 | . . | 77.9 | 0.79 | 0.17 |
| 8 | 102.6 | 55.7 | 44.8 | 45.6 | 46.7 | 55.0 | 84.2 | 1.16 | 0.19 |
| 16 | 112.7 | 63.6 | 58.6 | 52.4 | 54.3 | . . | 90.6 | 1.77 | . . |
| 32 | 121.2 | 72.0 | 65.0 | 61.8 | 62.9 | . . | 96.7 | 2.74 | . . |
| 64 | 129.0 | 82.0 | 76.0 | 72.8 | 73.1 | . . | 103.2 | . . | . . |
| 128 | 135.6 | 92.1 | 86.2 | 84.0 | 85.0 | 94.6 | 109.7 | . . | . . |
| 256 | 140.7 | 101.3 | 96.3 | 95.1 | 96.5 | . . | 116.0 | . . | . . |
| 512 | 144.1 | 109.0 | 106.1 | 105.5 | 108.0 | . . | . . | . . | . . |
| 1024 | 147.5 | 116.1 | 117.3 | 114.7 | 124.6 | 123.8 | . . | . . | . . |

TABLE VII—SPECIFIC CONDUCTIVITY OF SATURATED SOLUTIONS OF DIFFICULTY SOLUBLE SALTS AT 18°

| Substance | $10^6 \kappa$ | Remarks |
|---|---|---|
| $BaF_2$ | 1530.0 | |
| $SrF_2$ | 172.0 | |
| $CaF_2$ | 37.0 | |
| $MgF_2$ | 224.0 | |
| $PbF_2$ | 431.0 | |
| AgCl | 1.25 | Practically constant in dark, increases rapidly in daylight. |
| AgBr | 0.075 at 21.1° | |
| AgI | 0.0020 at 20.8° | |
| TlCl | 1514.0 | |
| TlBr | 192.2 | |
| TlI | 22.3 | |
| CuI | 1 to 5 | Increases rapidly on standing. |
| $HgI_2$ red | <0.2 | This is an upper limit. |
| $AgIO_3$ | 11.9 | |
| $Pb(IO_3)_2$ | 6.2 | |
| CuSCN | 0.1 to 0.4 | |
| $BaSO_4$ ppted | 2.4 | |
| $BaSO_4$ mineral | 2.8 | |
| $SrSO_4$ | 127.0 | No difference between ppted. and mineral |
| $CaSO_4+2H_2O$ | 1885.0 | |
| $PbSO_4$ | 32.4 | |
| $BaCrO_4$ | 3.20 | |
| $Ag_2CrO_4$ | 78.5 | |
| $PbCrO_4$ | 0.1 | |
| $BaCO_3$ | 25.5 | Probably hydrolized. See Gardner and Gerassimoff, Ztsch. phys. Chem. 48, 359 (1904). |
| $SrCO_3$ | 16.0 | |
| $CaCO_3$ ppted | 29.0 | |
| $CaCO_3$ calcite | 28.0 | |
| $CaCO_3$ aragonite | 32.6 | |
| $MgCO_3+3H_2O$ | 794.0 | |
| $Mg(OH)_2$ | 70.0 | |
| $Mg(OH)_2 \cdot 3Mg(CO_3)_2$ | 220.0 | |
| $MgC_2O_4 \cdot 2H_2O$ | 200.0 | |
| $BaC_2O_4 \cdot \frac{1}{2}H_2O$ (?) | 95.0 | |
| $BaC_2O_4 \cdot 2H_2O$ | 78.3 | |
| $BaC_2O_4$ | 70.2 | |
| $SrC_2O_4$ | 54.0 | |
| $CaC_2O_4+2H_2O$ | 27.0 | |
| $Ag_2SO_4$ | 25.5 | |
| $CaC_2O_4 \cdot H_2O$ | 9.6 | |
| $ZnC_2O_4+2H_2O$ | 8.0 | |
| $PbC_2O_4$ | 1.3 | |

TABLE VIII.—SPECIFIC CONDUCTIVITY AND CONCENTRATION OF SATURATED SOLUTIONS OF DIFFICULTLY SOLUBLE SALTS AT 20°.

| Substance. | $10^6 \kappa$ | Concentration Mg. per Liter. | Remarks. |
|---|---|---|---|
| $CaSO_4+2H_2O$ | 1968.0 | 2036.0 | |
| AgCl | 1.33 | 1.53 | |
| AgBr | 0.057 | 0.084 | |
| AgSCN | 0.096 | 0.137 | |
| $Ag_2CN$ | 0.154 | 0.403 | |
| AgCN | 0.19 | 0.22 | |
| $AgBrO_3$ | 663.9 | 1586.0 | |
| $AgIO_3$ | 14.05 | 43.5 | |
| $Ag_2O$ | 29.27 | 21.4 | |
| $Ag_2C_2O_4$ | 28.76 | 36.5 | |
| $Ag_3PO_4$ | 6.10 | 6.44 | |
| TlCl | 168.0 | 3256.0 | |
| TlBr | 220.9 | 476.0 | |
| TlI | 26.18 | 63.6 | |
| TlSCN | 140.0 | 3154.0 | |
| $TlBrO_3$ | 108.0 | 3493.0 | |

TABLE VIII.—(*Continued*).

| Substance. | $10^6.\kappa$ | Concentration Mg. per Liter. | Remarks. |
|---|---|---|---|
| $TlIO_3$ | 154.2 | 578.0 | |
| $Tl_4C_4O_4$ | 534.4 | 15770.0 | |
| $Tl_2S$ | 316.0 | 215.0 | |
| $PbCl_2$ | 5354.0 | 9613.0 | |
| $PbBr_2$ | 3697.0 | 8342.0 | |
| $PbI_2$ | 338.4 | 470.0 | |
| $Pb(SCN)_2$ | 2640.0 | 4500.0 | |
| $Pb(BrO_3)_2$ | 4635.0 | 13370.0 | |
| $Pb(IO_3)_2$ | 6.5 | 18.3 | |
| $PbC_2O_4$ | 1.52 | 1.80 | |
| $Pb_3(PO_4)_2$ | 0.14 | 0.135 | |
| $PbSO_4$ | 34.9 | 42.3 | |
| Lead oxide and hydroxide | 19.7 to 29.9 | 12.8 to 20.6 | Samples of varying composition. |
| Lead carbonate | 1.02 to 1.61 | 1.11 to 1.75 | " " " " |

TABLE IX.—SPECIFIC CONDUCTIVITY OF PURE LIQUIDS.

(I) Inorganic.

| Substance. | Temperature. | $\kappa^*$ or $l\times10^6$ | Authority. | Remarks. |
|---|---|---|---|---|
| Ammonia | −79.5° | 0.133* | Frenzel | |
| Ammonia | −60.0 | 0.195* | Frenzel | Temp. coef $\frac{1}{l_{-60^\circ}}\frac{dl}{dt}=0.019$ |
| Ammonia | −38.0 | 0.10* | Franklin and Kraus | |
| Ammonia | −34.0 | 7.1 | Cady | |
| Ammonia | −20.0 | 150.0 | Goodwin and Thompson | |
| Antimony trichloride | 80.0 | 109.0 | Walden | |
| Antimony tribromide | 100.0 | 50.0* | Schlundt | |
| Antimony triiodide | 175.0 | 110.0* | Schlundt | |
| Arsenic trichloride | 25.0 | 1.24 | Walden | |
| Arsenic trichloride | 17.0 | 3.8* | Schlundt | |
| Arsenic tribromide | 31.0 | 1.53* | Walden | |
| Arsenic tribromide | 35.0 | <2.0* | Schlundt | |
| Arsenic triiodide | 150.0 | 3.1* | Schlundt | |
| Hydrazine hydrate | 0.0 | 34 0* | Walden | |
| Nitric Acid | 0.0 | 15250.0 | Bouty | |
| Phosphorus trichloride | 20.0 | <1.0* | Schlundt | |
| Phosphoryl chloride | 25.0 | 1.7* to 2.2 | Walden | |
| Sulphur dioxide | 0 0 | 0.09 | Walden and Centnerszwer | |
| Sulphurous chloride | 25.0 | 2.0 | Walden | |
| Sulphuric acid | 25.0 | 7600.0* | Walden | |
| Sulphuric chlorhydrate | 25.0 | 160 0* | Walden | |
| Sulphuric chloride | 25.0 | 0.18 | Walden | |
| Sulphuryl chloride | 25.0 | 0.03* | Walden | |

(II) Organic.

| | | | | |
|---|---|---|---|---|
| *Acids :* | | | | |
| Formic | 15.0° | 12.3 | Novák | |
| Formic | 17.0 | 17.05 | Carrara and Levi | |
| Formic | 18 8 | 40.0 | Saposchnikoff | |
| Acetic | 15.0 | 0.0 | Whetham | |
| Acetic | 18.0 | 0.04 | Kohlrausch | |
| Acetic | 25 0 | 0.02* | Patten | |
| Propionic | 18.0 | 0.07 | Otten | |
| Butyric | 18.0 | 0.06 | Otten | |
| *iso*-Butyric | 18.0 | 0.05 | Otten | |
| Valerianic | 18.0 | 0.04 | Otten | |
| Capronic | 18.0 | 0.04 | Otten | |
| Hydrocyanic, see nitriles | | | | |
| Thioacetic | 25.0 | 2.69 | Walden† | |
| *Alcohols :* | | | | |
| Methyl | 15.0 | 0.93 | Holland | |
| Methyl | 18.0 | 1.2 | Völlmer | |
| Methyl | 18.0 | 1.8* | Dennhardt | |
| Methyl | 25.0 | 0.072* | Carrara | |
| Methyl | 25 0 | 1.45* | Walden† | |
| Methyl | 25.0 | 1 to 2 | Schall | |
| Methyl | 25.0 | 2.3 | Jones and Lindsay | |
| Methyl | 25.0 | 2.5* | Carrara and Levi | |
| Ethyl | 0.0 | 0.1487* | Walden† | |
| Ethyl | 18.0 | 0.11 | Völlmer | 0.062 after standing ½ year. |
| Ethyl | 18.0 | 0.126 | Pfeiffer | |
| Ethyl | 18.0 | 0.15 | Cohen | |

* Indicates reciprocal ohms.

TABLE IX.—(*Continued*).

| Substance. | Temperature. | $\kappa^{\infty}$ or $1/\times 10^6$ | Authority. | Remarks. |
|---|---|---|---|---|
| Ethyl | 18.0 | 0.15 | Wildermann | |
| Ethyl | 18.0 | 0.2 to 0.3 | Kohlrausch | |
| Ethyl | 25.0 | 0.1 | Schall | |
| Ethyl | 25.0 | 0.2 | Hantzsch and Voegelen | |
| Ethyl | 25.0 | 0.2 | Jones and Lindsay | |
| Ethyl | 25.0 | 0.1985° | Walden† | |
| Propyl | 15.2 | 0.08 to 0.26 | Schlamp | |
| Propyl | 25.0 | 0 08 | Jones and Lindsay | |
| Amyl | 17.0 | 0.069 | Hartwig | |
| *iso*-Amyl | 17.0 | 0.03 | Warburg | |
| *iso*-Amyl | 18.0 | 0.15° | Dennhardt | |
| *iso*-Amyl | 20.0 | 0.3 | Nernst | |
| *iso*-Amyl | 25.0 | 0.221 | Andrews and Ende | |
| Allyl | 25.0 | 6.5 | Lincoln | |
| Benzyl | 25.0 | 1.76 | Lincoln | |
| *Aldehydes:* | | | | |
| Acetaldehyde | 0.0 | 1.20° | Walden† | |
| Acetaldehyde | 0.0 | 2.7° | Walden† | |
| Paraldehyde | 25.0 | 0.34 | Lincoln | |
| Propionaldehyde | 0.0 | 0.698° | Walden† | |
| Propionaldehyde | 25.0 | 0.849° | Walden† | |
| *iso*-Valeraldehyde | 0.0 | 0.0794° | Walden† | |
| *iso*-Valeraldehyde | 25.0 | 0.0994° | Walden† | |
| Furfurol | 25.0 | 2.6° | Walden† | |
| Furfurol | 25.0 | 24.0 | Lincoln | |
| Benzaldehyde | 25.0 | 0.16° | Walden† | |
| Benzaldehyde | 25.0 | 0.45 | Kahlenberg and Lincoln | |
| Benzaldehyde | 25.0 | 1.0° | Fetter | |
| Salicylaldehyde | 0.0 | 0.100° | Walden† | |
| Salicylaldehyde | 25.0 | 0.163° | Walden† | |
| Salicylaldehyde | 25.0 | 5.98 | Lincoln | |
| Anisaldehyde | 0.0 | 0.0908° | Walden† | |
| Anisaldehyde | 25.0 | 0.1195° | Walden† | |
| *Esters:* | | | | |
| Methyl acetate | 25.0 | 3.37° | Fetter | |
| Ethyl acetate | 25.0 | 0.45 | Kahlenberg and Lincoln | |
| Ethyl aceto-acetate | 25.0 | 0.04 | Kahlenberg and Lincoln | |
| Methyl cyanacetate | 25.0 | 0.446° | Walden† | |
| Ethyl cyanacetate | 25.0 | 0.30° | Walden† | |
| Ethyl cyanacetate | 25.0 | 0.37 | Lincoln | |
| Ethyl monochloracetate | 25.0 | 1.7 | Lincoln | |
| Ethyl oxalate | 25.0 | 0.71 | Lincoln | |
| Methyl malonate | 0.0 | 0.0794° | Walden† | |
| Methyl malonate | 25.0 | 0.120° | Walden† | |
| Ethyl benzoate | 25.0 | 0.18 | Lincoln | |
| Ethyl benzoylacetate | 0.0 | 0.069° | Walden† | |
| Ethyl benzoylacetate | 25.0 | 0.090° | Walden† | |
| Methyl sulphate | 25.0 | 2.9° | Walden | |
| Methyl sulphate | 25.0 | 0.343° | Walden† | |
| *Acid derivatives:* | | | | |
| Acetic anhydride | 0.0 | 1.01° | Walden† | |
| *iso*-Butyric anhydride | 0.0 | 0.0944° | Walden† | |
| *iso*-Butyric anhydride | 25.0 | 0.1598° | Walden† | |
| Acetyl chloride | 25.0 | 0.953° | Walden† | |
| Acetyl bromide | 0.0 | 2.088° | Walden† | |
| Acetyl bromide | 25.0 | 3.377° | Walden† | |
| Bromacetyl bromide | 0.0 | 0 725° | Walden | |
| Formamide | 25.0 | 47.0° | Walden† | |
| Acetamide | 81.0 | 390.0° | Walden† | |
| *Nitriles:* | | | | |
| Cyanogen | 0.0 | <0.007 | Centnerszwer | Probably a non-conductor. |
| Hydrocyanic acid | 0.0 | 4.73° | Kahlenberg and Schlundt | |
| Hydrocyanic acid | 0.0 | 4.96 | Centnerszwer | |
| Acetonitrile | 0.0 | 0.3105° | Walden† | |
| Acetonitrile | 25.0 | 0.398° | Walden† | |
| Acetdinitrile | 25.0 | 2.0 | Dutoit and Friderich | |
| Propionitrile | 25.0 | 0.001° | Walden† | Commercial, 0.2 |
| Propionitrile | 25.0 | 2 0 | Dutoit and Friderich | |
| Butyronitrile | 25.0 | 1.2 | Dutoit and Friderich | |
| Hydroxyacetonitrile (Glycolic nitrile) | 0.0 | 5.16° | Walden† | |
| Hydroxyacetonitrile (Glycolic nitrile) | 25.0 | 8.43° | Walden† | |

TABLE IX.—(*Continued*).

| Substance. | Temperature. | $\kappa^0$ or $l/\times 10^6$ | Authority. | Remarks. |
|---|---|---|---|---|
| Hydroxypropionitrile (Lactic nitrile) . . . | 0.0 | 3.16° | Walden† | |
| Hydroxypropionitrile (Lactic nitrile) . . . | 25.0 | 4.94° | Walden† | |
| Ethylene cyanide . . . | 60.0 | 1.50° | Walden† | |
| Benzonitrile . . . . . | 25.0 | 1.9 | Lincoln | |
| Benzonitrile . . . . . | 25.0 | 3.31° | Walden† | |
| Benzonitrile . . . . . | 25.0 | 9.4° | Patten | |
| Benzyl cyanide . . . . | 26.0 | 0.40° | Walden† | |
| *Sulphocyanates and mustard oils :* | | | | |
| Methyl sulphocyanate . | 25.0 | 1.46° | Walden† | |
| Methyl sulphocyanate . | 25.0 | 7.38° | Kahlenberg | |
| Ethyl sulphocyanate . | 25.0 | 2.62° | Walden† | |
| hyl sulphocyanate . | 25.0 | 4.8° | Kahlenberg | |
| Amyl sulphocyanate . | 25.0 | 14.7° | Kahlenberg | |
| Methyl mustard oil . . | 50.0 | 0.33° | Walden† | |
| Ethyl mustard oil . . . | 25.0 | <0.363° | Kahlenberg | |
| Ethyl mustard oil . . . | 25.0 | 0.465° | Walden† | |
| Allyl mustard oil . . . | 25.0 | <0.043° | Kahlenberg | |
| *NO, $NO_2$ and $NO_3$ derivatives :* | | | | |
| Nitromethane . . . . . | 0.0 | 0.433° | Walden† | |
| Nitromethane . . . . . | 25.0 | 0.544° | Walden† | |
| Nitrobenzene . . . . . | 25.0 | 0.02° | Patten | |
| Nitrobenzene . . . . . | 25.0 | 0.35 | Kahlenberg and Lincoln | |
| *o*-Nitrotoluene . . . . . | 25.0 | 0.18 | Lincoln | |
| *m*-Nitrotoluene . . . . | 25.0 | 0.18 | Lincoln | |
| Amyl nitrite . . . . . | 25.0 | 0.18 | Lincoln | |
| Methyl nitrate . . . . | 25.0 | 4.52° | Patten | |
| Ethyl nitrate . . . . . | 0.0 | 0.44° | Walden† | |
| Dimethyl nitrosamine . | 25.0 | 29.5° | Walden† | |
| *Nitrogen bases :* | | | | |
| Amyl amine . . . . . | 25.0 | 0.082° | Kahlenberg and Ruhoff | |
| Aniline . . . . . | 20.0 | 0.06 | Nernst | |
| Pyridine . . . . . | 18.0 | 0.0 | Laszczynski and Goraki | $R^1 > 100{,}000$ ohms |
| Pyridine . . . . . | 25.0 | 0.75 | Lincoln | |
| Pyridine . . . . . | 25.0 | 0.96° | Carrara and Levi | |
| Piperidine . . . . . | 25.0 | 0.18 | Lincoln | |
| Quinoline . . . . . | 25.0 | 0.37 | Lincoln | |
| *Ketones :* | | | | |
| Acetone . . . . . | 18.0 | 0.0 | Laszczynski | $R^1 > 100{,}000$ ohms |
| Acetone . . . . . | 18.0 | 0.09 | Lemme | |
| Acetone . . . . . | 18.0 | 0.147 | Cattaneo | |
| Acetone . . . . . | 25.0 | 0.227° | Walden† | |
| Acetone . . . . . | 25.0 | 0.6° | Carrara and Levi | |
| Acetylacetone . . . . . | 25.0 | 15.9° | Walden† | |
| Methylpropylketone . | 25.0 | 0.95 | Lincoln | |
| Acetophenone . . . . . | 25.0 | 0.18 | Lincoln | |

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Bouty: *Compt. rend.* **106**, 595 (1888).
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Carrara and Levi: *Ibid.*, **32**, 11, 36 (1902)
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Holland: *Ibid.*, **50**, 263 (1893).
Jones and Lindsay: *Am. Chem. J.*, **28**, 329 (1902).

† R indicates the resistance, no conductivity being given.

TABLE VIII.—(*Continued*).

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Walden : *Ztsch. anorg Chem.*, 25, 209 (1900); 29, 371 (1902); *Ztsch. phys. Chem.*, 43, 385 (1903); 46, 129 (1903). †Only minimum values from this last paper are given in the above table.
Walden and Centnerszwer : *Ztsch. phys. Chem.*, 39, 513 (1902).
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Whetham, *Phil. Mag.* (5) 44, 4 (1897).
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TABLE X—ATOMIC WEIGHTS OF THE PRINCIPAL ELEMENTS ACCORDING TO THE REPORT OF THE INTERNATIONAL COMMITTEE, 1905.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Ag | 107.93 | Cd | 112.4 | I | 126.97 | Pb | 206.9 |
| Al | 27.1 | Cl | 35.45 | K | 39.15 | Pt | 194.8 |
| As | 75.0 | Co | 59.0 | Li | 7.03 | Rb | 85.5 |
| Au | 197.2 | Cr | 52.1 | Mg | 24.36 | S | 32.06 |
| B | 11.0 | Cs | 132.9 | Mn | 55.0 | Sb | 120.2 |
| Ba | 137.4 | Cu | 63.6 | N | 14.04 | Si | 28.4 |
| Bi | 208.5 | F | 19. | Na | 23.05 | Sn | 119.0 |
| Br | 79.96 | Fe | 55.9 | Ni | 58.7 | Sr | 87.6 |
| C | 12.00 | H | 1.008 | O | 16.00 | Tl | 204. |
| Ca | 40.1 | Hg | 200.0 | P | 31.0 | Zn | 65.4 |

TABLE XI—EQUIVALENT WEIGHTS, *W*, (½O=8) AND ELECTROCHEMICAL EQUIVALENTS, *E*, IN MILLIGRAMS PER AMPERE-SECOND OF THE PRINCIPAL IONS.

| *Cations* | *W* | *E* | *Anions* | *W* | *E* |
|---|---|---|---|---|---|
| H | 1.008 | 0.01043 | Cl | 35.45 | 0.3671 |
| K | 39.15 | 0.4054 | Br | 79.96 | 0.8279 |
| Na | 23.05 | 0.2387 | I | 126.97 | 1.3146 |
| Li | 7.03 | 0.07279 | F | 19. | 0.1967 |
| $NH_4$ | 18.07 | 0.1871 | OH | 17.01 | 0.1761 |
| Ag | 107.93 | 1.1175 | CN | 26.04 | 0.2696 |
| Tl | 204.1 | 2.113 | $NO_3$ | 62.04 | 0.6424 |
| | | | $ClO_3$ | 83.45 | 0.8641 |
| ½Ba | 68.7 | 0.7113 | $BrO_3$ | 127.96 | 1.3249 |
| ½Sr | 43.8 | 0.4535 | $IO_3$ | 174.97 | 1.8116 |
| ½Ca | 20.05 | 0.2076 | $CHO_2$ | 45.01 | 0.4660 |
| ½Mg | 12.18 | 0.1261 | $C_2H_3O_2$ | 59.02 | 0.6111 |
| ½Zn | 32.7 | 0.3386 | | | |
| ½Cd | 56.2 | 0.5819 | ½O | 8.00 | 0.08282 |
| ½Cu | 31.8 | 0.3293 | ½S | 16.03 | 0.1660 |
| ½Fe | 27.95 | 0.2894 | $\frac{1}{2}SO_4$ | 48.03 | 0.4973 |
| ½Mn | 27.5 | 0.2847 | $\frac{1}{2}CrO_4$ | 58.05 | 0.6011 |
| ½Ni | 29.35 | 0.3039 | $\frac{1}{2}CO_3$ | 30.00 | 0.3106 |
| ½Pb | 103.45 | 1.0711 | $\frac{1}{2}C_2O_4$ | 44.00 | 0.4555 |

## TABLE XII—OBACH'S TABLE FOR WHEATSTONE BRIDGE VALUES OF $\frac{a}{1-a}$ CORRESPONDING TO $a$

| $a$. | 1 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|---|---|
| 00 | 0.0000 | 0010 | 0020 | 0030 | 0040 | 0050 | 0060 | 0070 | 0081 | 0091 |
| 01 | 0101 | 0111 | 0121 | 0131 | 0142 | 0152 | 0163 | 0173 | 0183 | 0194 |
| 02 | 0204 | 0215 | 0225 | 0235 | 0246 | 0256 | 0267 | 0277 | 0288 | 0299 |
| 03 | 0309 | 0320 | 0331 | 0341 | 0352 | 0363 | 0373 | 0384 | 0395 | 0406 |
| 04 | 0417 | 0428 | 0438 | 0449 | 0460 | 0471 | 0482 | 0493 | 0504 | 0515 |
| 05 | 0526 | 0537 | 0549 | 0560 | 0571 | 0582 | 0593 | 0604 | 0616 | 0627 |
| 06 | 0638 | 0650 | 0661 | 0672 | 0684 | 0695 | 0707 | 0718 | 0730 | 0741 |
| 07 | 0753 | 0764 | 0776 | 0787 | 0799 | 0811 | 0823 | 0834 | 0846 | 0858 |
| 08 | 0870 | 0881 | 0893 | 0905 | 0917 | 0929 | 0941 | 0953 | 0965 | 0977 |
| 09 | 0989 | 1001 | 1013 | 1025 | 1038 | 1050 | 1062 | 1074 | 1086 | 1099 |
| 10 | 0.1111 | 1123 | 1136 | 1148 | 1161 | 1173 | 1186 | 1198 | 1211 | 1223 |
| 11 | 1236 | 1249 | 1261 | 1274 | 1287 | 1299 | 1312 | 1325 | 1338 | 1351 |
| 12 | 1364 | 1377 | 1390 | 1403 | 1416 | 1429 | 1442 | 1455 | 1468 | 1481 |
| 13 | 1494 | 1507 | 1521 | 1534 | 1547 | 1561 | 1574 | 1587 | 1601 | 1614 |
| 14 | 1628 | 1641 | 1655 | 1669 | 1682 | 1696 | 1710 | 1723 | 1737 | 1751 |
| 15 | 1765 | 1779 | 1792 | 1806 | 1820 | 1834 | 1848 | 1862 | 1876 | 1891 |
| 16 | 1905 | 1919 | 1933 | 1947 | 1962 | 1976 | 1990 | 2005 | 2019 | 2034 |
| 17 | 2048 | 2063 | 2077 | 2092 | 2107 | 2121 | 2136 | 2151 | 2165 | 2180 |
| 18 | 2195 | 2210 | 2225 | 2240 | 2255 | 2270 | 2285 | 2300 | 2315 | 2330 |
| 19 | 2346 | 2361 | 2376 | 2392 | 2407 | 2422 | 2438 | 2453 | 2469 | 2484 |
| 20 | 0.2500 | 2516 | 2531 | 2547 | 2563 | 2579 | 2594 | 2610 | 2626 | 2642 |
| 21 | 2658 | 2674 | 2690 | 2706 | 2723 | 2739 | 2755 | 2771 | 2788 | 2804 |
| 22 | 2820 | 2837 | 2853 | 2870 | 2887 | 2903 | 2920 | 2937 | 2953 | 2970 |
| 23 | 2987 | 3004 | 3021 | 3038 | 3055 | 3072 | 3089 | 3106 | 3123 | 3141 |
| 24 | 3158 | 3175 | 3193 | 3210 | 3228 | 3245 | 3263 | 3280 | 3298 | 3316 |
| 25 | 3333 | 3351 | 3369 | 3387 | 3405 | 3423 | 3441 | 3459 | 3477 | 3495 |
| 26 | 3514 | 3532 | 3550 | 3569 | 3587 | 3605 | 3624 | 3643 | 3661 | 3680 |
| 27 | 3699 | 3717 | 3736 | 3755 | 3774 | 3793 | 3812 | 3831 | 3850 | 3870 |
| 28 | 3889 | 3908 | 3928 | 3947 | 3966 | 3986 | 4006 | 4025 | 4045 | 4065 |
| 29 | 4085 | 4104 | 4124 | 4144 | 4164 | 4184 | 4205 | 4225 | 4245 | 4265 |
| 30 | 0.4286 | 4306 | 4327 | 4347 | 4368 | 4388 | 4409 | 4430 | 4451 | 4472 |
| 31 | 4493 | 4514 | 4535 | 4556 | 4577 | 4599 | 4620 | 4641 | 4663 | 4684 |
| 32 | 4706 | 4728 | 4749 | 4771 | 4793 | 4815 | 4837 | 4859 | 4881 | 4903 |
| 33 | 4925 | 4948 | 4970 | 4993 | 5015 | 5038 | 5060 | 5083 | 5106 | 5121 |
| 34 | 5152 | 5175 | 5198 | 5221 | 5244 | 5267 | 5291 | 5314 | 5337 | 5369 |
| 35 | 5385 | 5408 | 5432 | 5456 | 5480 | 5504 | 5528 | 5552 | 5576 | 5601 |
| 36 | 5625 | 5649 | 5674 | 5699 | 5723 | 5748 | 5773 | 5798 | 5823 | 5848 |
| 37 | 5873 | 5898 | 5924 | 5949 | 5974 | 6000 | 6026 | 6051 | 6077 | 6103 |
| 38 | 6129 | 6155 | 6181 | 6207 | 6234 | 6260 | 6287 | 6313 | 6340 | 6367 |
| 39 | 6393 | 6420 | 6447 | 6474 | 6502 | 6529 | 6556 | 6584 | 6611 | 6639 |
| 40 | 0.6667 | 6694 | 6722 | 6750 | 6779 | 6807 | 6835 | 6863 | 6892 | 6921 |
| 41 | 6949 | 6978 | 7007 | 7036 | 7065 | 7094 | 7123 | 7153 | 7182 | 7212 |
| 42 | 7241 | 7271 | 7301 | 7331 | 7361 | 7391 | 7421 | 7452 | 7483 | 7513 |
| 43 | 7544 | 7575 | 7606 | 7637 | 7668 | 7699 | 7731 | 7762 | 7794 | 7825 |
| 44 | 7857 | 7889 | 7921 | 7953 | 7986 | 8018 | 8051 | 8083 | 8116 | 8149 |
| 45 | 8182 | 8215 | 8248 | 8282 | 8315 | 8349 | 8382 | 8416 | 8450 | 8484 |
| 46 | 8519 | 8553 | 8587 | 8622 | 8657 | 8692 | 8727 | 8762 | 8797 | 8832 |
| 47 | 8868 | 8904 | 8939 | 8975 | 9011 | 9048 | 9084 | 9120 | 9157 | 9194 |
| 48 | 9231 | 9268 | 9305 | 9342 | 9380 | 9417 | 9455 | 9493 | 9531 | 9569 |
| 49 | 9608 | 9646 | 9685 | 9724 | 9763 | 9802 | 9841 | 9881 | 9920 | 9960 |
| 50 | 1.0000 | 1.0040 | 1.0080 | 1.0121 | 1.0161 | 1.0202 | 1.0243 | 1.0284 | 1.0325 | 1.0367 |
| 51 | 1.0408 | 1.0450 | 1.0492 | 1.0534 | 1.0576 | 1.0619 | 1.0661 | 1.0704 | 1.0747 | 1.0790 |
| 52 | 1.0833 | 1.0877 | 1.0921 | 1.0964 | 1.1008 | 1.1053 | 1.1097 | 1.1142 | 1.1186 | 1.1231 |
| 53 | 1.1277 | 1.1322 | 1.1368 | 1.1413 | 1.1459 | 1.1505 | 1.1552 | 1.1598 | 1.1645 | 1.1692 |
| 54 | 1.1739 | 1.1786 | 1.1834 | 1.1882 | 1.1930 | 1.1978 | 1.2026 | 1.2075 | 1.2124 | 1.2173 |
| 55 | 1.2222 | 1.2272 | 1.2321 | 1.2371 | 1.2422 | 1.2472 | 1.2523 | 1.2573 | 1.2624 | 1.2676 |
| 56 | 1.2727 | 1.2779 | 1.2831 | 1.2883 | 1.2936 | 1.2989 | 1.3041 | 1.3095 | 1.3148 | 1.3202 |
| 57 | 1.3256 | 1.3310 | 1.3364 | 1.3419 | 1.3474 | 1.3529 | 1.3585 | 1.3641 | 1.3697 | 1.3753 |
| 58 | 1.3810 | 1.3866 | 1.3923 | 1.3981 | 1.4038 | 1.4096 | 1.4155 | 1.4213 | 1.4272 | 1.4331 |
| 59 | 1.4390 | 1.4450 | 1.4510 | 1.4570 | 1.4631 | 1.4691 | 1.4752 | 1.4814 | 1.4876 | 1.4938 |

TABLE XII.—(*Continued*).

| *a* | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|---|---|
| 60 | 1.500 | 1.506 | 1.513 | 1.519 | 1.525 | 1.532 | 1.538 | 1.545 | 1.551 | 1.558 |
| 61 | 1.564 | 1.571 | 1.577 | 1.584 | 1.591 | 1.597 | 1.604 | 1.611 | 1.618 | 1.625 |
| 62 | 1.632 | 1.639 | 1.646 | 1.653 | 1.660 | 1.667 | 1.674 | 1.681 | 1.688 | 1.695 |
| 63 | 1.703 | 1.710 | 1.717 | 1.725 | 1.732 | 1.740 | 1.747 | 1.755 | 1.762 | 1.770 |
| 64 | 1.778 | 1.786 | 1.793 | 1.801 | 1.809 | 1.817 | 1.825 | 1.833 | 1.841 | 1.849 |
| 65 | 1.857 | 1.865 | 1.874 | 1.882 | 1.890 | 1.899 | 1.907 | 1.915 | 1.924 | 1.933 |
| 66 | 1.941 | 1.950 | 1.959 | 1.967 | 1.976 | 1.985 | 1.994 | 2.003 | 2.012 | 2.021 |
| 67 | 2.030 | 2.040 | 2.049 | 2.058 | 2.067 | 2.077 | 2.086 | 2.096 | 2.106 | 2.115 |
| 68 | 2.125 | 2.135 | 2.145 | 2.155 | 2.165 | 2.175 | 2.185 | 2.195 | 2.205 | 2.215 |
| 69 | 2.226 | 2.236 | 2.247 | 2.257 | 2.268 | 2.279 | 2.289 | 2.300 | 2 311 | 2.322 |
| 70 | 2.333 | 2.344 | 2.356 | 2.367 | 2.378 | 2.390 | 2.401 | 2.413 | 2.425 | 2.436 |
| 71 | 2.448 | 2.460 | 2.472 | 2.484 | 2.497 | 2.509 | 2.521 | 2.534 | 2.546 | 2.559 |
| 72 | 2.571 | 2.584 | 2.597 | 2.610 | 2.623 | 2.636 | 2.650 | 2.663 | 2.676 | 2.690 |
| 73 | 2.704 | 2.717 | 2.731 | 2.745 | 2.759 | 2.774 | 2.788 | 2.802 | 2.817 | 2.831 |
| 74 | 2.846 | 2.861 | 2.876 | 2.891 | 2.906 | 2.922 | 2.937 | 2.953 | 2.968 | 2.984 |
| 75 | 3.000 | 3.016 | 3.032 | 3.049 | 3 065 | 3 082 | 3.098 | 3.115 | 3.132 | 3.149 |
| 76 | 3 167 | 3.184 | 3.202 | 3.219 | 3.237 | 3.255 | 3.274 | 3.292 | 3.310 | 3.329 |
| 77 | 3.348 | 3.367 | 3.386 | 3.405 | 3.425 | 3.444 | 3 464 | 3.484 | 3.505 | 3.525 |
| 78 | 3.545 | 3.566 | 3.587 | 3.608 | 3.630 | 3.651 | 3.673 | 3.695 | 3.717 | 3.739 |
| 79 | 3.762 | 3.785 | 3.808 | 3.831 | 3.854 | 3.878 | 3.902 | 3.926 | 3.950 | 3.975 |
| 80 | 4.000 | 4.025 | 4.051 | 4.076 | 4.102 | 4.128 | 4.155 | 4.181 | 4 208 | 4.236 |
| 81 | 4.263 | 4.291 | 4.319 | 4.348 | 4.376 | 4.405 | 4.435 | 4.464 | 4.495 | 4.525 |
| 82 | 4.556 | 4.587 | 4 618 | 4.650 | 4.682 | 4.714 | 5.747 | 4.780 | 4.814 | 4.848 |
| 83 | 4.882 | 4.917 | 4.952 | 4 988 | 5.024 | 5 061 | 5.098 | 5.135 | 5.173 | 5.211 |
| 84 | 5.250 | 5.289 | 5.329 | 5.369 | 5.410 | 5.452 | 5.494 | 5 536 | 5.579 | 5.623 |
| 85 | 5.667 | 5.711 | 5 757 | 5.803 | 5.849 | 5.897 | 5.944 | 5.993 | 6.042 | 6.092 |
| 86 | 6.143 | 6.194 | 6.246 | 6.299 | 6.353 | 6.407 | 6.463 | 6 519 | 6.576 | 6.634 |
| 87 | 6 692 | 6.752 | 6.813 | 6.874 | 6.937 | 7.000 | 7.065 | 7.130 | 7.197 | 7.264 |
| 88 | 7.333 | 7.403 | 7.475 | 7.547 | 7.621 | 7.696 | 7.772 | 7.850 | 7.929 | 8.009 |
| 89 | 8.091 | 8.174 | 8.259 | 8.346 | 8.434 | 8.524 | 8.615 | 8.709 | 8.804 | 8.901 |
| 90 | 9.00 | 9.10 | 9.20 | 9.31 | 9.42 | 9.53 | 9.64 | 9.75 | 9.87 | 9.99 |
| 91 | 10.11 | 10.24 | 10.36 | 10.49 | 10.63 | 10 76 | 10.90 | 11.05 | 11.20 | 11.35 |
| 92 | 11.50 | 11.66 | 11.82 | 11.99 | 12.16 | 12.33 | 12.51 | 12.70 | 12.89 | 13.08 |
| 93 | 13.29 | 13.49 | 13.71 | 13.93 | 14.15 | 14.38 | 14.63 | 14 87 | 15.13 | 15.39 |
| 94 | 15.67 | 15.95 | 16.24 | 16.54 | 16.86 | 17.18 | 17.52 | 17.87 | 18.23 | 18.61 |
| 95 | 19.00 | 19.41 | 19.83 | 20.28 | 20.74 | 21.22 | 21.73 | 22.26 | 22.81 | 23.39 |
| 96 | 24.00 | 24.64 | 25.32 | 26.03 | 26.78 | 27.57 | 28.41 | 29.30 | 30.25 | 31.26 |
| 97 | 32.33 | 33.48 | 34.71 | 36.04 | 37.46 | 39.00 | 40.67 | 42.48 | 44.45 | 46.62 |
| 98 | 49.00 | 51.63 | 54.56 | 57.82 | 61.50 | 65.67 | 70.43 | 75.92 | 82.33 | 89.91 |
| 99 | 99.00, | 110.1 | 124.0 | 141.9 | 165.7 | 199.0 | 249.0 | 332.3 | 499.0 | 999.0 |

TABLE XIII.—OBACH'S LOGARITHMIC TABLE FOR WHEATSTONE BRIDGE.

LOGARITHM OF $\frac{a}{1-a}$ CORRESPONDING TO *a*.

| *a*. | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|---|---|
| 00 | —∞ | 7.0004 | 3019 | 4784 | 6038 | 7011 | 7808 | 8481 | 9066 | 9582 |
| 01 | 8.0044 | 8.0462 | 0844 | 1196 | 1523 | 1827 | 2111 | 2379 | 2632 | 2871 |
| 02 | 3098 | 3314 | 3521 | 3718 | 3908 | 4089 | 4264 | 4433 | 4595 | 4752 |
| 03 | 4903 | 5050 | 5193 | 5331 | 5465 | 5595 | 5722 | 5846 | 5966 | 6083 |
| 04 | 6198 | 6310 | 6419 | 6526 | 6630 | 6732 | 6832 | 6930 | 7026 | 7120 |
| 05 | 7212 | 7303 | 7392 | 7479 | 7565 | 7649 | 7732 | 7814 | 7894 | 7973 |
| 06 | 8050 | 8127 | 8202 | 8276 | 8349 | 8421 | 8492 | 8562 | 8631 | 8699 |
| 07 | 8766 | 8832 | 8898 | 8962 | 9026 | 9089 | 9151 | 9213 | 9274 | 9334 |
| 08 | 9393 | 9452 | 9510 | 9567 | 9624 | 9680 | 9736 | 9790 | 9845 | 9899 |
| 09 | 9952 | 9.0005 | 0057 | 0109 | 0160 | 0211 | 0261 | 0311 | 0360 | 0409 |
| 10 | 9.0458 | 0506 | 0553 | 0600 | 0647 | 0694 | 0740 | 0785 | 0831 | 0875 |
| 11 | 0920 | 0964 | 1008 | 1052 | 1095 | 1138 | 1180 | 1222 | 1264 | 1306 |
| 12 | 1347 | 1388 | 1429 | 1469 | 1509 | 1549 | 1589 | 1628 | 1667 | 1706 |
| 13 | 1744 | 1783 | 1821 | 1858 | 1896 | 1933 | 1970 | 2007 | 2044 | 2080 |
| 14 | 2116 | 2152 | 2188 | 2224 | 2259 | 2294 | 2329 | 2364 | 2398 | 2433 |

TABLE XIII.—(*Continued*).

| d | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|---|---|
| 15 | 9.2467 | 2501 | 2534 | 2568 | 2602 | 2635 | 2668 | 2701 | 2733 | 2766 |
| 16 | 2798 | 2831 | 2863 | 2895 | 2926 | 2958 | 2989 | 3021 | 3052 | 3083 |
| 17 | 3114 | 3144 | 3175 | 3205 | 3236 | 3266 | 3296 | 3326 | 3355 | 3385 |
| 18 | 3415 | 3444 | 3473 | 3502 | 3531 | 3560 | 3589 | 3618 | 3646 | 3674 |
| 19 | 3703 | 7313 | 3759 | 3787 | 3815 | 3842 | 3870 | 3898 | 3925 | 3952 |
| 20 | 9.3979 | 4006 | 4033 | 4060 | 4087 | 4114 | 4140 | 4167 | 4193 | 4220 |
| 21 | 4246 | 4272 | 4298 | 4324 | 4350 | 4376 | 4401 | 4427 | 4452 | 4478 |
| 22 | 4503 | 4529 | 4554 | 4579 | 4604 | 4629 | 4654 | 4678 | 4703 | 4728 |
| 23 | 4753 | 4777 | 4801 | 4826 | 4850 | 4874 | 4898 | 4922 | 4946 | 4970 |
| 24 | 4994 | 5018 | 5041 | 5065 | 5089 | 5112 | 5136 | 5159 | 5182 | 5206 |
| 25 | 5229 | 5252 | 5275 | 5298 | 5321 | 5344 | 5367 | 5389 | 5412 | 5435 |
| 26 | 5457 | 5480 | 5502 | 5525 | 5547 | 5570 | 5592 | 5614 | 5636 | 5658 |
| 27 | 5680 | 5702 | 5724 | 5746 | 5768 | 5790 | 5812 | 5833 | 5855 | 5877 |
| 28 | 5898 | 5920 | 5941 | 5963 | 5984 | 6005 | 6027 | 6048 | 6069 | 6090 |
| 29 | 6111 | 6132 | 6153 | 6174 | 6195 | 6216 | 6237 | 6258 | 6279 | 6300 |
| 30 | 9.6320 | 6341 | 6362 | 6382 | 6403 | 6423 | 6444 | 6464 | 6484 | 6505 |
| 31 | 6525 | 6545 | 6566 | 6586 | 6606 | 6626 | 6646 | 6666 | 6686 | 6706 |
| 32 | 6726 | 6746 | 6766 | 6786 | 6806 | 6826 | 6846 | 6865 | 6885 | 6905 |
| 33 | 6924 | 6944 | 6964 | 6983 | 7003 | 7022 | 7042 | 7061 | 7081 | 7100 |
| 34 | 7119 | 7139 | 7158 | 7177 | 7197 | 7216 | 7235 | 7254 | 7273 | 7292 |
| 35 | 7312 | 7331 | 7350 | 7369 | 7388 | 7407 | 7426 | 7445 | 7463 | 7482 |
| 36 | 7501 | 7520 | 7539 | 7558 | 7576 | 7595 | 7614 | 7633 | 7651 | 7670 |
| 37 | 7689 | 7707 | 7726 | 7744 | 7763 | 7782 | 7800 | 7819 | 7837 | 7855 |
| 38 | 7874 | 7892 | 7911 | 7929 | 7948 | 7966 | 7984 | 8003 | 8021 | 8039 |
| 39 | 8057 | 8076 | 8094 | 8112 | 8130 | 8148 | 8167 | 8185 | 8203 | 8221 |
| 40 | 9.8239 | 8257 | 8275 | 8293 | 8311 | 8329 | 8347 | 8365 | 8383 | 8401 |
| 41 | 8419 | 8437 | 8455 | 8473 | 8491 | 8509 | 8527 | 8545 | 8563 | 8580 |
| 42 | 8598 | 8616 | 8634 | 8652 | 8669 | 8687 | 8705 | 8723 | 8740 | 8758 |
| 43 | 8776 | 8794 | 8811 | 8829 | 8847 | 8864 | 8882 | 8900 | 8917 | 8935 |
| 44 | 8953 | 8970 | 8988 | 9005 | 9023 | 9041 | 9058 | 9076 | 9093 | 9111 |
| 45 | 9128 | 9146 | 9164 | 9181 | 9199 | 9216 | 9234 | 9251 | 9269 | 9286 |
| 46 | 9304 | 9321 | 9339 | 9356 | 9374 | 9391 | 9408 | 9426 | 9443 | 9461 |
| 47 | 9478 | 9496 | 9513 | 9531 | 9548 | 9565 | 9583 | 9600 | 9618 | 9635 |
| 48 | 9652 | 9670 | 9687 | 9705 | 9722 | 9739 | 9757 | 9774 | 9791 | 9809 |
| 49 | 9826 | 9844 | 9861 | 9878 | 9896 | 9913 | 9931 | 9948 | 9965 | 9983 |
| 50 | 0.0000 | 0017 | 0035 | 0052 | 0069 | 0087 | 0104 | 0122 | 0139 | 0156 |
| 51 | 0174 | 0191 | 0209 | 0226 | 0243 | 0261 | 0278 | 0295 | 0313 | 0330 |
| 52 | 0348 | 0365 | 0382 | 0400 | 0417 | 0435 | 0452 | 0469 | 0487 | 0504 |
| 53 | 0522 | 0539 | 0557 | 0574 | 0592 | 0609 | 0626 | 0644 | 0661 | 0679 |
| 54 | 0696 | 0714 | 0731 | 0749 | 0766 | 0784 | 0801 | 0819 | 0836 | 0854 |
| 55 | 0872 | 0889 | 0907 | 0924 | 0942 | 0959 | 0977 | 0995 | 1012 | 1030 |
| 56 | 1047 | 1065 | 1083 | 1100 | 1118 | 1136 | 1153 | 1171 | 1189 | 1206 |
| 57 | 1224 | 1242 | 1260 | 1277 | 1295 | 1313 | 1331 | 1348 | 1366 | 1384 |
| 58 | 1402 | 1420 | 1437 | 1455 | 1473 | 1491 | 1509 | 1527 | 1545 | 1563 |
| 59 | 1581 | 1599 | 1617 | 1635 | 1653 | 1671 | 1689 | 1707 | 1725 | 1743 |
| 60 | 0.1761 | 1779 | 1795 | 1815 | 1833 | 1852 | 1870 | 1888 | 1906 | 1924 |
| 61 | 1943 | 1961 | 1979 | 1997 | 2016 | 2034 | 2052 | 2071 | 2089 | 2108 |
| 62 | 2126 | 2145 | 2163 | 2181 | 2200 | 2218 | 2237 | 2256 | 2274 | 2293 |
| 63 | 2311 | 2330 | 2349 | 2367 | 2386 | 2405 | 2424 | 2442 | 2461 | 2480 |
| 64 | 2499 | 2518 | 2537 | 2555 | 2574 | 2593 | 2612 | 2631 | 2650 | 2669 |
| 65 | 2688 | 2708 | 2727 | 2746 | 2765 | 2784 | 2803 | 2823 | 2842 | 2861 |
| 66 | 2881 | 2900 | 2919 | 2939 | 2958 | 2978 | 2997 | 3017 | 3036 | 3056 |
| 67 | 3076 | 3095 | 3115 | 3135 | 3154 | 3174 | 3194 | 3214 | 3234 | 3254 |
| 68 | 3274 | 3294 | 3314 | 3334 | 3354 | 3374 | 3394 | 3414 | 3434 | 3455 |
| 69 | 3475 | 3495 | 3516 | 3536 | 3556 | 3577 | 3597 | 3618 | 3638 | 3659 |
| 70 | 0.3680 | 3700 | 3721 | 3742 | 3763 | 3784 | 3805 | 3826 | 3847 | 3868 |
| 71 | 3889 | 3910 | 3931 | 3952 | 3973 | 3995 | 4016 | 4037 | 4059 | 4080 |
| 72 | 4102 | 4123 | 4145 | 4167 | 4188 | 4210 | 4232 | 4254 | 4276 | 4298 |
| 73 | 4320 | 4342 | 4364 | 4386 | 4408 | 4430 | 4453 | 4475 | 4498 | 4520 |
| 74 | 4543 | 4565 | 4588 | 4611 | 4633 | 4656 | 4679 | 4702 | 4725 | 4748 |

TABLE XIII.—(*Continued*).

| θ | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|---|---|
| 75 | 0.4771 | 4794 | 4818 | 4841 | 4864 | 4888 | 4911 | 4935 | 4959 | 4982 |
| 76 | 5006 | 5030 | 5054 | 5078 | 5102 | 5126 | 5150 | 5174 | 5199 | 5223 |
| 77 | 5248 | 5272 | 5297 | 5322 | 5346 | 5371 | 5396 | 5421 | 5446 | 5471 |
| 78 | 5497 | 5522 | 5548 | 5573 | 5599 | 5624 | 5650 | 5676 | 5702 | 5728 |
| 79 | 5754 | 5780 | 5807 | 5833 | 5860 | 5886 | 5913 | 5940 | 5969 | 5994 |
| 80 | 0.6021 | 6048 | 6075 | 6102 | 6130 | 6158 | 6185 | 6213 | 6241 | 6269 |
| 81 | 6297 | 6326 | 6354 | 6382 | 6411 | 6440 | 6469 | 6498 | 6527 | 6556 |
| 82 | 6585 | 6615 | 6645 | 6674 | 6704 | 6734 | 6764 | 6795 | 6825 | 6856 |
| 83 | 6886 | 6917 | 6948 | 6979 | 7011 | 7042 | 7074 | 7105 | 7137 | 7169 |
| 84 | 7202 | 7234 | 7267 | 7299 | 7332 | 7365 | 7398 | 7432 | 7466 | 7499 |
| 85 | 7533 | 7567 | 7602 | 7636 | 7671 | 7706 | 7741 | 7776 | 7812 | 7848 |
| 86 | 7884 | 7920 | 7956 | 7993 | 8030 | 8067 | 8104 | 8142 | 8179 | 8217 |
| 87 | 8256 | 8294 | 8333 | 8372 | 8411 | 8451 | 8491 | 8531 | 8571 | 8612 |
| 88 | 8653 | 8694 | 8736 | 8778 | 8820 | 8862 | 8905 | 8948 | 8992 | 9036 |
| 89 | 9080 | 9125 | 9169 | 9215 | 9260 | 9306 | 9353 | 9400 | 9447 | 9494 |
| 90 | 0.9542 | 9591 | 9640 | 9689 | 9739 | 9789 | 9840 | 9891 | 9943 | 9995 |
| 91 | 1.0048 | 0101 | 0155 | 0210 | 0264 | 0320 | 0376 | 0433 | 0490 | 0548 |
| 92 | 0607 | 0666 | 0726 | 0787 | 0849 | 0911 | 0974 | 1038 | 1102 | 1168 |
| 93 | 1234 | 1301 | 1369 | 1438 | 1508 | 1579 | 1651 | 1724 | 1798 | 1873 |
| 94 | 1950 | 2027 | 2106 | 2186 | 2268 | 2351 | 2435 | 2521 | 2608 | 2697 |
| 95 | 279 | 288 | 297 | 307 | 317 | 327 | 337 | 347 | 358 | 369 |
| 96 | 380 | 392 | 403 | 415 | 428 | 440 | 453 | 467 | 481 | 495 |
| 97 | 510 | 525 | 541 | 557 | 574 | 591 | 609 | 628 | 648 | 669 |
| 98 | 690 | 713 | 737 | 762 | 789 | 817 | 848 | 880 | 916 | 954 |
| 99 | 996 | 2.042 | 093 | 152 | 219 | 299 | 396 | 522 | 698 | 3.000 |

TABLE XIV—LOGARITHMS

| N | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | Diff |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 10 | 0000 | 0043 | 0086 | 0128 | 0170 | 0212 | 0253 | 0294 | 0334 | 0374 | 42 |
| 11 | 0414 | 0453 | 0492 | 0531 | 0569 | 0607 | 0645 | 0682 | 0719 | 0755 | 38 |
| 12 | 0792 | 0828 | 0864 | 0899 | 0934 | 0969 | 1004 | 1038 | 1072 | 1106 | 35 |
| 13 | 1139 | 1173 | 1206 | 1239 | 1271 | 1303 | 1335 | 1367 | 1399 | 1430 | 32 |
| 14 | 1461 | 1492 | 1523 | 1553 | 1584 | 1614 | 1644 | 1673 | 1703 | 1732 | 30 |
| 15 | 1761 | 1790 | 1818 | 1847 | 1875 | 1903 | 1931 | 1959 | 1987 | 2014 | 28 |
| 16 | 2041 | 2068 | 2095 | 2122 | 2148 | 2175 | 2201 | 2227 | 2253 | 2279 | 26 |
| 17 | 2304 | 2330 | 2355 | 2380 | 2405 | 2430 | 2455 | 2480 | 2504 | 2529 | 25 |
| 18 | 2553 | 2577 | 2601 | 2625 | 2648 | 2672 | 2695 | 2718 | 2742 | 2765 | 24 |
| 19 | 2788 | 2810 | 2833 | 2856 | 2878 | 2900 | 2923 | 2945 | 2967 | 2989 | 22 |
| 20 | 3010 | 3032 | 3054 | 3075 | 3096 | 3118 | 3139 | 3160 | 3181 | 3201 | 21 |
| 21 | 3222 | 3243 | 3263 | 3284 | 3304 | 3324 | 3345 | 3365 | 3385 | 3404 | 20 |
| 22 | 3424 | 3444 | 3464 | 3483 | 3502 | 3522 | 3541 | 3560 | 3579 | 3598 | 19 |
| 23 | 3617 | 3636 | 3655 | 3674 | 3692 | 3711 | 3729 | 3747 | 3766 | 3784 | 19 |
| 24 | 3802 | 3820 | 3838 | 3856 | 3874 | 3892 | 3909 | 3927 | 3945 | 3962 | 18 |
| 25 | 3979 | 3997 | 4014 | 4031 | 4048 | 4065 | 4082 | 4099 | 4116 | 4133 | 17 |
| 26 | 4150 | 4166 | 4183 | 4200 | 4216 | 4232 | 4249 | 4265 | 4281 | 4298 | 16 |
| 27 | 4314 | 4330 | 4346 | 4362 | 4378 | 4393 | 4409 | 4425 | 4440 | 4456 | 16 |
| 28 | 4472 | 4487 | 4502 | 4518 | 4533 | 4548 | 4564 | 4579 | 4594 | 4609 | 15 |
| 29 | 4624 | 4639 | 4654 | 4669 | 4683 | 4698 | 4713 | 4728 | 4742 | 4757 | 15 |
| 30 | 4771 | 4786 | 4800 | 4814 | 4829 | 4843 | 4857 | 4871 | 4886 | 4900 | 14 |
| 31 | 4914 | 4928 | 4942 | 4955 | 4969 | 4983 | 4997 | 5011 | 5024 | 5038 | 14 |
| 32 | 5051 | 5065 | 5079 | 5092 | 5105 | 5119 | 5132 | 5145 | 5159 | 5172 | 13 |
| 33 | 5185 | 5198 | 5211 | 5224 | 5237 | 5250 | 5263 | 5276 | 5289 | 5302 | 13 |
| 34 | 5315 | 5328 | 5340 | 5353 | 5366 | 5378 | 5391 | 5403 | 5416 | 5428 | 13 |

TABLE XIV.—(*Continued*).

| N | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | Diff |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 35 | 5441 | 5453 | 5465 | 5478 | 5490 | 5502 | 5514 | 5527 | 5539 | 5551 | 12 |
| 36 | 5563 | 5575 | 5587 | 5599 | 5611 | 5623 | 5635 | 5647 | 5658 | 5670 | 12 |
| 37 | 5682 | 5694 | 5705 | 5717 | 5729 | 5740 | 5752 | 5763 | 5775 | 5787 | 12 |
| 38 | 5798 | 5809 | 5821 | 5832 | 5843 | 5855 | 5856 | 5877 | 5888 | 5899 | 11 |
| 39 | 5911 | 5922 | 5933 | 5944 | 5955 | 5966 | 5977 | 5988 | 5999 | 6010 | 11 |
| 40 | 6021 | 6031 | 6042 | 6053 | 6064 | 6075 | 6085 | 6096 | 6107 | 6117 | 11 |
| 41 | 6128 | 6138 | 6149 | 6160 | 6170 | 6180 | 6191 | 6201 | 6212 | 6222 | 10 |
| 42 | 6232 | 6243 | 6253 | 6263 | 6274 | 6284 | 6294 | 6304 | 6314 | 6325 | 10 |
| 43 | 6335 | 6345 | 6355 | 6365 | 6375 | 6385 | 6395 | 6405 | 6415 | 6425 | 10 |
| 44 | 6435 | 6444 | 6454 | 6464 | 6474 | 6484 | 6493 | 9503 | 6513 | 6522 | 10 |
| 45 | 6532 | 6542 | 6551 | 6561 | 6571 | 6580 | 6590 | 6599 | 6609 | 6618 | 10 |
| 46 | 6628 | 6637 | 6646 | 6656 | 6665 | 6675 | 6684 | 6693 | 6702 | 6712 | 9 |
| 47 | 6721 | 6730 | 6739 | 6749 | 6758 | 6767 | 6776 | 6785 | 6794 | 6803 | 9 |
| 48 | 6812 | 6821 | 6830 | 6839 | 6848 | 6857 | 6866 | 6875 | 6884 | 6893 | 9 |
| 49 | 6902 | 6911 | 6920 | 6928 | 6937 | 6946 | 6955 | 6964 | 6972 | 4981 | 9 |
| 50 | 6990 | 6998 | 7007 | 7016 | 7024 | 7033 | 7042 | 7050 | 7059 | 7067 | 9 |
| 51 | 7076 | 7084 | 7093 | 7101 | 7110 | 7118 | 7126 | 7135 | 7143 | 7152 | 8 |
| 52 | 7160 | 7168 | 7177 | 7185 | 7193 | 7202 | 7210 | 7218 | 7226 | 7235 | 8 |
| 53 | 7243 | 7251 | 7259 | 7267 | 7275 | 7284 | 7292 | 7300 | 7308 | 7316 | 8 |
| 54 | 7324 | 7332 | 7340 | 7348 | 7356 | 7364 | 7372 | 7380 | 7388 | 7396 | 8 |
| 55 | 7404 | 7412 | 7419 | 7427 | 7435 | 7443 | 7451 | 7459 | 7466 | 7474 | 8 |
| 56 | 7482 | 7490 | 7497 | 7505 | 7513 | 7520 | 7528 | 7536 | 7543 | 7551 | 8 |
| 57 | 7559 | 7566 | 7574 | 7582 | 7589 | 7597 | 7604 | 7612 | 7619 | 7627 | 8 |
| 58 | 7634 | 7642 | 7648 | 7657 | 7664 | 7672 | 7679 | 7686 | 7694 | 7701 | 7 |
| 59 | 7709 | 7716 | 7723 | 7731 | 7738 | 7745 | 7752 | 7760 | 7767 | 7774 | 7 |
| 60 | 7782 | 7789 | 7796 | 7803 | 7810 | 7818 | 7825 | 7832 | 7839 | 7846 | 7 |
| 61 | 7853 | 7860 | 7868 | 7875 | 7882 | 7889 | 7896 | 7903 | 7910 | 7917 | 7 |
| 62 | 7924 | 7931 | 7938 | 7945 | 7952 | 7959 | 7966 | 7973 | 7980 | 7987 | 7 |
| 63 | 7993 | 8000 | 8007 | 8014 | 8021 | 8028 | 8035 | 8041 | 8048 | 8055 | 7 |
| 64 | 8062 | 8069 | 8075 | 8082 | 8089 | 8096 | 8102 | 8109 | 8116 | 8122 | 7 |
| 65 | 8129 | 8136 | 8142 | 8149 | 8156 | 8162 | 8169 | 9179 | 8182 | 8189 | 7 |
| 66 | 8195 | 8202 | 8209 | 8215 | 8222 | 8228 | 8235 | 8241 | 8248 | 8254 | 7 |
| 67 | 8261 | 8267 | 8274 | 8280 | 8287 | 8293 | 8299 | 8306 | 8312 | 8319 | 6 |
| 68 | 8325 | 8331 | 8338 | 8344 | 8351 | 8357 | 8363 | 8370 | 8376 | 8382 | 6 |
| 69 | 8388 | 8395 | 8401 | 8407 | 8414 | 8420 | 8426 | 8432 | 8439 | 8445 | 6 |
| 70 | 8451 | 8457 | 8463 | 8470 | 8476 | 8482 | 8488 | 8494 | 8500 | 8506 | 6 |
| 71 | 8513 | 8519 | 8525 | 8531 | 8537 | 8543 | 8549 | 8555 | 8561 | 8567 | 6 |
| 72 | 8573 | 8579 | 8585 | 8591 | 8597 | 8603 | 8609 | 8615 | 8621 | 8627 | 6 |
| 73 | 8633 | 8639 | 8645 | 8651 | 8657 | 8663 | 8669 | 8675 | 8681 | 8686 | 6 |
| 74 | 8692 | 8698 | 8704 | 8710 | 8716 | 8722 | 8727 | 8733 | 8739 | 8745 | 6 |
| 75 | 8751 | 8756 | 8762 | 8768 | 8774 | 8770 | 8785 | 8791 | 8797 | 8802 | 6 |
| 76 | 8808 | 8814 | 8820 | 8825 | 8831 | 8837 | 8842 | 8848 | 8854 | 8859 | 6 |
| 77 | 8865 | 8871 | 8676 | 8882 | 8887 | 8893 | 8899 | 8904 | 8910 | 8915 | 6 |
| 78 | 8921 | 8927 | 8932 | 8938 | 8943 | 8949 | 8954 | 8960 | 8965 | 8971 | 6 |
| 79 | 8976 | 8982 | 8987 | 8993 | 8998 | 9004 | 9009 | 9015 | 9020 | 9025 | 5 |
| 80 | 9031 | 9036 | 9042 | 9047 | 9053 | 9058 | 9063 | 9069 | 9074 | 9079 | 5 |
| 81 | 9085 | 9090 | 9096 | 9101 | 9106 | 9112 | 9117 | 9122 | 9128 | 9133 | 5 |
| 82 | 9138 | 9143 | 9149 | 9154 | 9159 | 9165 | 9170 | 9175 | 9180 | 9186 | 5 |
| 83 | 9191 | 9196 | 9201 | 9206 | 9212 | 9217 | 9222 | 9227 | 9232 | 9238 | 5 |
| 84 | 9243 | 9248 | 9253 | 9258 | 9263 | 9269 | 9274 | 9279 | 9284 | 9289 | 5 |
| 85 | 9294 | 9299 | 9304 | 9309 | 9315 | 9320 | 9325 | 9330 | 9335 | 9340 | 5 |
| 86 | 9345 | 9350 | 9355 | 9360 | 9365 | 9370 | 9375 | 9380 | 9385 | 9390 | 5 |
| 87 | 9395 | 9400 | 9405 | 9410 | 9415 | 9420 | 9425 | 9430 | 9435 | 9440 | 5 |
| 88 | 9445 | 9450 | 9455 | 9460 | 9465 | 9469 | 9474 | 9479 | 9484 | 9489 | 5 |
| 89 | 9494 | 9499 | 9504 | 9509 | 9513 | 9518 | 9523 | 9528 | 9533 | 9538 | 5 |

TABLE XIV.—(*Continued*).

| N | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 7 | 9 | Diff. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 90 | 9542 | 9547 | 9552 | 9557 | 9562 | 9566 | 9571 | 9576 | 9581 | 9586 | 5 |
| 91 | 9590 | 9595 | 9600 | 9605 | 9609 | 9614 | 9619 | 9624 | 9628 | 9633 | 5 |
| 92 | 9638 | 9643 | 9647 | 9652 | 9657 | 9661 | 9666 | 9671 | 9675 | 9680 | 5 |
| 93 | 9685 | 9689 | 9694 | 9699 | 9703 | 9708 | 9713 | 9717 | 9722 | 9727 | 5 |
| 94 | 9731 | 9736 | 9741 | 9745 | 9750 | 9754 | 9759 | 9763 | 9768 | 9773 | 5 |
| 95 | 9777 | 9782 | 9786 | 9791 | 9795 | 9800 | 9805 | 9809 | 9814 | 9818 | 5 |
| 96 | 9823 | 9827 | 9832 | 9836 | 9841 | 9845 | 9850 | 9854 | 9859 | 9863 | 5 |
| 97 | 9868 | 9872 | 9877 | 9881 | 9886 | 9890 | 9894 | 9899 | 9903 | 9908 | 4 |
| 98 | 9912 | 9917 | 9921 | 9926 | 9930 | 9934 | 9939 | 9943 | 9948 | 9952 | 4 |
| 99 | 9956 | 9961 | 9965 | 9969 | 9974 | 9978 | 9983 | 9987 | 9991 | 9996 | 4 |
| 100 | 0000 | 0043 | 0087 | 0130 | 0173 | 0217 | 0260 | 0303 | 0346 | 0389 | 43 |
| 101 | 0432 | 0475 | 0518 | 0561 | 0604 | 0647 | 0689 | 0732 | 0775 | 0817 | 43 |
| 102 | 0860 | 0903 | 0945 | 0988 | 1030 | 1072 | 1115 | 1157 | 1199 | 1242 | 42 |
| 103 | 1284 | 1326 | 1368 | 1410 | 1452 | 1494 | 1536 | 1578 | 1620 | 1662 | 42 |
| 104 | 1703 | 1745 | 1787 | 1828 | 1870 | 1912 | 1953 | 1995 | 2036 | 2078 | 42 |
| 105 | 2119 | 2160 | 2202 | 2243 | 2284 | 2325 | 2366 | 2407 | 2449 | 2490 | 41 |
| 106 | 2531 | 2572 | 2612 | 2653 | 2694 | 2735 | 2776 | 2816 | 2857 | 2898 | 41 |
| 107 | 2938 | 2979 | 3019 | 3060 | 3100 | 3141 | 3181 | 3222 | 3262 | 3302 | 40 |
| 108 | 3342 | 3383 | 3423 | 3463 | 3503 | 3543 | 3583 | 3623 | 3663 | 3703 | 40 |
| 109 | 3743 | 3782 | 3822 | 3862 | 3902 | 3941 | 3981 | 4021 | 4060 | 4100 | 40 |
| 110 | 4139 | 4179 | 4218 | 4258 | 4297 | 4336 | 4376 | 4415 | 4454 | 4493 | 39 |

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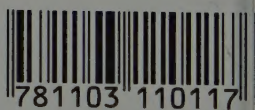

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